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DEVELOPMENT OF STANDARD METHODS FOR THE COLLECTION AND ANALYSIS OF PRECIPITATION

Authors:
Mark E. Peden
Susan R. Bachman
Carla Jo Brennan
Brigita Demir
Kenni O. James
Brian W. Kaiser
Jacqueline M. Lockard
Jane E. Rothert
Jackie Sauer
Loretta M. Skowron
Michael J. Slater

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Mark E. Peden
Principal Investigator

Contract Number CR810780-01

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch

Environmental Monitoring and Support Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, OH 45268

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Champaign, Illinois 61820

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To provide the scientific community with a set of standardized procedures for the collection and analysis of wet precipitation samples, an analytical methods manual for use in acid deposition studies has been developed. This manual includes detailed methods documentation for the major inorganic constituents of interest in wet deposition as well as guidelines for the collection, preservation, and processing of samples. The importance of a comprehensive quality assurance program is emphasized for all aspects of a precipitation chemistry measurement system. The analytical methodologies include flame atomic absorption spectrophotometry, ion selective electrode, automated colorimetry, ion chromatography, and titrimetric procedures. These methods were selected for inclusion based on their sensitivities, accuracy, and freedom from significant chemical and physical interferences. The instrumentation required for these methods is available in most laboratories involved with water analyses so that the procedures described will be useful to as many researchers as possible. The adoption of standard test procedures will lead to greater comparability between laboratories reporting precipitation chemistry data and will improve the reliability of data interpretation efforts.

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FOREWORD

Environmental measurements are required to determine the quality of the ambient waters and the character of waste effluents. The Environmental Monitoring and Support Laboratory--Cincinnati conducts research to:

1. Develop and evaluate methods to measure the presence and concentration of physical, chemical, and radiological pollutants in water, wastewater, bottom sediments, and solid waste.

2. Investigate methods for the concentration, recovery, and identification of viruses, bacteria, and other microbiological organisms in water, and determine the responses of aquatic organisms to water quality.

3. Develop and operate an Agency-wide quality assurance program to assure standardization and quality control of systems for monitoring water and wastewater.

4. Develop and operate a computerized system for instrument automation leading to improved data collection, analysis, and quality control.

This research project was designed to produce a methods manual of standardized procedures containing single laboratory precision and bias statements that can be used to analyze wet acid deposition samples.

Robert L. Booth, Director
Environmental Monitoring and Support
Laboratory--Cincinnati

ABSTRACT

Local, state, regional, and national precipitation chemistry networks have been established during the last twenty-five years in an effort to assess temporal and spatial patterns in atmospheric deposition. These networks have been implemented with varied objectives but they all involve the collection and chemical analysis of precipitation. Interpretation of the data generated from these various measurement programs has been complicated by the different sampling and analytical protocols that have been employed. This is particularly true of historical data sets that do not include complete information on the analytical methodologies used, bias and precision of reported chemical results, or quality assurance practices. These procedural differences, combined with a lack of adequate documentation, have resulted in nonuniform data sets that make trend analysis difficult.

To provide the scientific community with a set of standardized procedures for the collection and analysis of precipitation samples, the Illinois State Water Survey has developed an analytical methods manual for use in acid deposition studies. This manual includes detailed methods documentation for the major inorganic constituents of interest in wet deposition as well as guidelines for the collection, preservation, and processing of samples. The importance of a comprehensive quality assurance program is emphasized for all aspects of a precipitation chemistry measurement system. The analytical methodologies include flame atomic absorption spectrophotometry, ion selective electrode, automated colorimetry, ion chromatography, and titrimetric procedures. These methods were selected for inclusion based on their sensitivities, accuracy, and freedom from significant chemical and physical interferences. The instrumentation required for these methods is available in most laboratories involved with water analyses so that the procedures described will be useful to as many researchers as possible. The adoption of standard test procedures will lead to greater comparability between laboratories reporting precipitation chemistry data and will improve the reliability of data interpretation efforts.

INTRODUCTION

Standard test procedures for the chemical analysis of wet deposition are not currently available to the scientific community. As a result, different analytical techniques historically have been used to produce precipitation chemistry data. These techniques often lack the necessary sensitivity and accuracy for measurement of the trace constituents characteristic of wet deposition samples. Comparison of these data for spatial and temporal trend analyses is therefore difficult and may lead to false conclusions.

An extensive literature review was conducted at the onset of this project to compile an inventory of recent and historical precipitation chemistry monitoring programs. Information on study objectives, sampling protocols, handling procedures, chemical constituents, analytical methodologies, and quality assurance practices was synthesized to develop an overview of the current status of wet deposition monitoring. It was apparent from this inventory that differences in sampling periods were necessary depending on the monitoring objectives. Weekly sampling may be acceptable for assessing annual deposition patterns whereas sequential samples within a single event may be important for obtaining information on scavenging processes. Our approach, therefore, was to develop sampling guidelines that would meet as many study objectives as possible. The sampler types and collection vessels commonly used were also tabulated. Most of the monitoring networks are already using similar equipment and collection containers for the analysis of the major inorganic species in wet deposition so that a consensual standard is already in place. Our efforts have focused on developing recommendations for the selection, cleaning, and handling of the collection vessels.

The sample handling and processing protocols used for wet deposition analyses were also addressed. Minimizing sample contamination and ensuring the integrity of samples after collection was the primary focus in this area. Guidelines for recommended holding times for each of the species detailed in the methods documentation were developed based on ion stability studies conducted at the Illinois State Water Survey and other laboratories. Recommended storage containers and temperatures were also included in this work. Physical means of sample preservation by filtration was included as a mechanism for stabilizing constituents affected by the presence of alkaline particulates and/or biological activity. These guidelines are ion specific since wet deposition samples are characterized by both conservative and nonconservative chemical species.

The first step in selecting candidate procedures for inclusion in this methods manual was to tabulate the methodologies currently being used by major precipitation chemistry laboratories. In most cases, these techniques were similar although differences were apparent in reporting units, method detection limits, precision, and bias. Quality assurance protocols were extremely varied as were the procedures used for presenting quality control data. These disparities emphasized the need for a set of standardized procedures for both analytical determinations and quality assurance data reporting.

The median concentration of total dissolved species in wet deposition samples from the National Atmospheric Deposition Program (NADP)/National Trends Network (NTN) is approximately 90 microequivalents/liter. Methods selection, therefore, must take into consideration the fact that the majority of analytes in wet deposition are present at concentrations below one milligram/liter. Analytical techniques characterized by sufficiently low method detection limits are crucial to the accurate determination of these trace constituents. Cumulative percentile concentration data were tabulated from the 1984 NADP/NTN Program for use as a guide in both methods selection and for recommending appropriate calibration standards in the methods documentation. This systematic approach to method selection ensures that the chemical data generated will be of maximum utility to many users.

The documentation and formalization of quality assurance protocols is an integral component of the methods development process. This includes quality control at the sampling site, in the laboratory, and in data reporting. This manual focuses on the specific control procedures that are necessary to obtain data with known bias and precision. The use of blind audit solutions, internal quality control check solutions, control charts, analyte spikes, and performance audits should all be incorporated into the standard operating procedures (SOP) for laboratories engaged in wet deposition measurements.

The methods contained in this report are comprehensive in their coverage and include detailed descriptions of the instrumentation, reagents, procedures, quality control protocols, and data reporting requirements for each analyte. The documentation has been prepared according to the guidelines set forth by the USEPA Environmental Monitoring and Support Laboratory (EMSL) in Cincinnati, Ohio (Kopp, 1983). These guidelines are patterned after the format used by the American Society for Testing and Materials (ASTM, 1983) and are accepted as the standard to be used in formalizing analytical test procedures.

Standard methods of documented bias and precision are now available for the major inorganic species in wet deposition. The general methodologies described are already being used by many precipitation chemistry laboratories, but complete documentation has not previously been available. By incorporating these test methods as standard operating procedures, laboratories involved with wet deposition measurements will be producing data of similar quality. This will result in easier data interpretation by various users and should improve the reliability of wet deposition measurements.

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GLOSSARY

Item	Abbreviation	Definition
Accuracy		The difference between the mean value and the true value when the latter is known or assumed. The concept of accuracy includes both bias (systematic error) and precision (random error).
Bias		A persistent positive or negative deviation of the measured value from the true value, due to the experimental method. In practice, it is expressed as the difference between the mean value obtained from repetitive testing of a homogenous sample and the accepted true value: Bias = measured value - true value
Control Limits	CL	Statistically derived values that limit the range of acceptable random error in a measurement process. They consist of an upper and lower range of acceptable values that are defined as ±3s from the mean.
Field Blank	FB	An aliquot of reagent water or equivalent neutral reference material treated as a sample in all aspects, including exposure to a collection vessel, holding time, preservatives, and all other sample processing and analysis protocols.
Field Duplicates	FD	Two samples taken at the same time and place under identical conditions that are treated alike throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
Laboratory Duplicates	LD	Two aliquots of the same sample treated identically throughout a laboratory analytical procedure. Analyses of laboratory duplicates indicate the precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.

Laboratory Spike		A known volume of method analyte that is added to a sample. The concentration of analyte spiked into the sample usually approximates the expected concentration of that analyte in the unspiked sample. The difference in concentration between the spiked and the unspiked sample is used to calculate a method percent recovery.
Mean Bias		$\frac{\sum \text{bias for each sample}}{\text{total number of replicates (n)}}$
Mean Percent Recovery		$\frac{\sum \text{percent recovery for each sample}}{\text{total number of replicates (n)}}$
Method Detection Limit	MDL	The minimum concentration of an analyte that can be reported with 99% confidence that the value is above zero. The MDL is operationally defined as: $MDL = st_{(n-1,1-\alpha = 0.99)}$ (1) where: s = standard deviation of repetitive measurements (≥ 7) of a solution containing the analyte at a concentration near the MDL. $t_{(n-1,1-\alpha = 0.99)}$ = student's t value for a one-tailed test appropriate for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom.
Percent Bias		The difference between the mean value obtained by repeated testing of a homogenous sample and the accepted true value expressed as a percentage of the true value: $\% \text{ Bias} = 100 \times [(V_m - V_t)/V_t]$ where: V_m = measured value V_t = true value

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(1) Glaser, J.A., D.L. Foerst, G.D. McKee, S.A. Quave, and W.L. Budde. "Trace Analyses for Wastewaters". Environmental Science and Technology, 1981, Vol. 15, No. 12. pp. 1426-1435.

Percent Recovery		An estimate of the bias of an analytical method determined from analyte spikes of natural samples. The percent recovery is calculated as: $\%\ \text{Recovery} = 100 \times [(a - b)/c]$ where: a = measured concentration of spiked sample b = measured concentration of unspiked sample c = calculated spike concentration
Performance Evaluation Sample	PES	A sample containing known concentrations of method analytes unknown to the analyst. Results of laboratory analyses of these samples are used to statistically determine the bias and precision that can be expected when a method is performed by a competent analyst.
Precision		The degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the value obtained about the mean value. It is often reported as a sample standard deviation (s).
Quality Control Check Sample	QCS	A sample containing known concentrations of analytes prepared by the analyst or a laboratory other than the laboratory performing the analysis. The performing laboratory uses this sample to demonstrate that it can obtain acceptable results with procedures to be used to analyze wet deposition samples. Analyte true values are known by the analyst.
Relative Standard Deviation	RSD	The standard deviation expressed as a percentage. $RSD = 100 \times (s/\overline{x})$ where: s = sample standard deviation $\overline{x}$ = mean value
Sensitivity		The method signal response per unit of analyte.

Standard Deviation	s	A number that represents the dispersion of values around their mean, calculated as: $s = \sqrt{\frac{\Sigma(x_i - \bar{x})^2}{n - 1}}$ where: x_i = each individual value $\bar{x}$ = average of all values n = number of values
Statistical Control		The description of a measurement process that is characterized solely by random errors.
Traceability		The ability to verify a measurement or solution with known standards from the National Bureau of Standards, Washington, DC.
Warning Limits	WL	Limits used in quality control charts to indicate that the analytical procedure is close to being out of statistical control. They consist of an upper and lower range of values that are defined as ±2s from the mean value.
Zero Standard		A calibration standard used to set the instrument response to zero. It contains all of the matrix components of the remaining calibrants except the method analyte.

SAMPLE COLLECTION

The sample collection protocols used for the determination of major inorganic ions in wet deposition samples are influenced by the study objectives as well as economic and logistical constraints. The availability of qualified field personnel, adequate sources of electrical power, and funds for automated collection devices are all factors in the selection of sampling protocols. The benefits and limitations of various sampling schemes have been thoroughly discussed in the literature. The appended list of references relating to the collection of wet deposition samples has been compiled to aid the reader when selecting and evaluating sample collection procedures. General guidelines that should be considered when designing a wet deposition measurement program are discussed in the following sections.

COLLECTOR DESIGN

Wet deposition samples can be collected using bulk or wet-only design collectors. Bulk sampling refers to the collection of both wet and dry components of atmospheric deposition. The bulk sampling system typically consists of a bucket or funnel and bottle configuration that is open to the atmosphere during both precipitation events and dry periods. The funnel and bottle design is frequently used with a water trap in the tubing leading from the funnel to the collection bottle to minimize sample evaporation. Open bucket collectors are susceptible to evaporation, particularly under warm weather conditions or long exposure periods. The influence of dry deposition inputs to bulk samples is dependent not only on the ion being determined, but also on the meteorological conditions and location of the sample collector. Windy and dusty conditions during a bulk sampling period will result in higher solution concentrations of terrestrial components such as calcium and magnesium compared to a wet-only collection device. The dissolution of these alkaline materials can lead to additional changes in sample chemistry prior to analysis. Bulk sampling procedures can be used, however, for studies that focus on estimating total atmospheric inputs.

Wet-only collection devices minimize evaporation and the influence of dry deposition by utilizing an electronic sensing mechanism that exposes the collection vessel to the atmosphere only during precipitation events. The stability of samples collected with this type of device is also enhanced by the exclusion of slowly dissolving terrestrial components (Peden and Skowron, 1978). In order to effectively minimize evaporation and dry deposition inputs, a wet-only sampler should be equipped with a motor-driven, reciprocating cover that fits tightly over the top of the collection vessel during dry periods. The pressure of the cover should be strong enough to sustain a tight seal under high wind conditions and the surface of the lid that is in direct contact with the lip of the collection vessel must be constructed of an inert, non-contaminating polyolefin material. The reciprocating cover should be designed to minimize the accumulation of snow or ice during winter operation to prevent a malfunction of the drive motor. A rain gauge should be installed at the collection site to continuously monitor the volume of precipitation collected by a standard rain gauge compared to the volume collected in the sampler. An event recorder, triggered by the opening and closing of the sampler cover, is also recommended to diagnose malfunctions in the operation of the collector drive motor and sensing mechanism.

SITING CRITERIA

Collection sites for regional or background precipitation chemistry studies should be located at least 100 meters from routine air, ground, or water traffic. Overhead obstructions such as power lines or trees that can interfere with sample collection should be avoided. Maintain a horizontal distance between the sampling site and any large obstruction (i.e. building, radio antenna) of at least twice the height of the obstructing object. The ground surface of the collection site should be firm and covered with grass or similar vegetative cover. Periodically check the distance between obstructions such as growing trees or newly erected structures and the collection site. For a more complete list of siting criteria refer to Topol et al. (1985) and NADP (1984). Install the collector parallel to the wind direction that is characteristic of precipitation events. Place the sampler such that the collection vessel is upwind of the reciprocating cover and sensor mechanism.

Locate the rain gauge/event recorder near the collector with a horizontal distance of at least two meters between each instrument. Position the rain gauge parallel to both the collector and the direction of the prevailing winds to minimize any potential influence on the chemical quality of the precipitation.

COLLECTION VESSELS

All collection buckets, liners, funnel/bottle apparatuses, and storage bottles should be constructed from a non-contaminating material that will not adsorb the inorganic ions of interest. High density (linear) polyethylene, which has been shown to be a suitable collection and storage material, is most widely used for the collection and storage of wet deposition samples. Other plastic materials such as polypropylene, conventional (low density) polyethylene, and tetrafluoroethylene have been used successfully as well. All containers that will be used for sample collection or storage should be evaluated for adsorption/desorption properties on a continual basis since the purity of plastic products can vary among manufacturers and between different production runs from the same manufacturer. The evaluation of the collection vessel should include the cap or lid that is used to seal the container after collection. Gasket materials and cap liners that are used to ensure a watertight seal are potential sources of contamination that must also be investigated.

Thoroughly rinse all collection surfaces with ASTM Type II water prior to use. Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyolefin matrix and be slowly leached back into the sample. Alkaline detergents may also leave residues that can affect the sample chemistry. Wear particle-free, noncontaminating gloves whenever handling clean buckets or bucket liners.

Cap collection bottles after cleaning to prevent contamination from airborne contaminants. Air dry collection buckets and liners in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket or liner interior by any method other than air drying under a clean air workstation. Monitor the cleaning procedure by pouring a volume of reagent water that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentrations of the parameters that will be measured in wet deposition. If any of the analyte concentrations exceed the method detection limit (MDL), a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

SAMPLING FREQUENCY

The frequency of sampling is determined by the study objectives. Event, daily, and weekly sampling schedules are the most commonly used. Sequential samples taken within a single event are also used in studies focusing on precipitation scavenging processes. Collection periods of longer than one week are generally not recommended because of the potential for sample degradation and evaporation. For a more thorough discussion of sampling frequency considerations, refer to the appended references.

SAMPLE COLLECTION AND HANDLING

When servicing the collection equipment, always approach the sampler from the downwind side to prevent possible contamination from clothing, hair, or dust fragments. Do not touch any of the collection surfaces when removing or installing the collection vessel. Cap or seal all samples at the time of collection to prevent contamination or loss of sample during transit to a processing facility. Collection vessels should be brought to the sampling site in clean plastic bags and installed immediately after the bag has been removed. The reciprocating cover of wet-only samplers should be inspected each time the sampler is serviced to ensure that a tight seal is maintained between the collection vessel rim and the cover. The underside of the cover should be cleaned with ASTM Type II water on at least a monthly basis to prevent the buildup of dust or dirt that could result in sample contamination. Whenever samples are collected, check the sensor mechanism on the collector for proper operation. For more details on recommended collector operation and maintenance, refer to the NADP Instruction Manual for Site Operation (1982).

Field personnel responsible for the collection of samples should be instructed in the procedures that are required to operate a precipitation chemistry measurement site. In addition to operation and troubleshooting of the collection equipment, site operators should be aware of the careful handling techniques that are required to prevent sample contamination. Periodic evaluations of field personnel performance are recommended to ensure that the sample collection and handling protocols are being followed.

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QUALITY ASSURANCE

Wet deposition samples are characterized by very low concentration levels of dissolved constituents. The median ionic strength of samples collected from the National Atmospheric Deposition Program (NADP) - National Trends Network (NTN) during 1984 was only 90 microequivalents per liter. The dilute nature of precipitation samples requires that a rigorous quality assurance (QA) program be followed to monitor and control the variables that affect sample representativeness. A quality assurance program for precipitation chemistry measurements should include all aspects of sample collection, handling, chemical analysis, and data management. Both the theoretical and practical aspects of QA program planning for wet deposition measurement systems are thoroughly discussed in the appended references.

The methods documentation provided in this manual includes specific laboratory quality control procedures that should be followed by analysts performing chemical determinations of precipitation samples. These guidelines represent a minimum level of quality control that is necessary to ensure data quality. Additional control procedures may be required depending on the design of the measurement program.

The verification of laboratory analyses using ion balance and specific conductance calculations is an important quality assurance tool that should be used by all laboratories engaged in wet deposition measurements. If the major ions in a solution have been determined (SO_4^{-2}, NO_3^-, HCO_3^-, Cl^-, Ca^{+2}, Mg^{+2}, Na^+, K^+, H^+, and NH_4^+), the equivalent concentrations of measured anions should equal the sum of the measured cations. The calculation of an ion ratio or ion balance can be used to detect analytical errors as well as a major ion that has not been detected. Ion balances should be determined for all samples and the results used to identify samples for chemical reanalysis (Peden, 1983). Table 1 provides a comparison chart of four methods that are commonly used by precipitation chemists to determine an ion balance. Columns one and two represent an ion balance calculation expressed as a percentage; columns three and four represent equivalent ratios. The formulas used to calculate each balance are provided under the respective headings. Although each method provides similar information, the use of different calculation procedures can lead to confusion when comparing quality assurance data from various laboratories. The American Society For Testing and Materials (ASTM) recommends the use of the following calculation in determining ion balance data (ASTM, 1983):

$$\text{Percentage error} = \frac{\text{Cations} - \text{Anions}}{\text{Cations} + \text{Anions}} \times 100$$

This formula is similar to the calculation shown in the second column of Table 1 with the order of cations and anions reversed in the numerator. The use of the ASTM method for calculation of ion balance data is recommended for all laboratories engaged in precipitation chemistry analyses to facilitate comparison between researchers.

Reanalysis criteria can be established in several ways using ion balance data. Peden (1983) described the use of ion percent difference data in conjunction with the total ionic strength of the sample to develop a three-level criteria that takes into account the higher variability characteristic of very dilute (< 50 microequivalents/liter total ion strength) samples (Table 2). ASTM Method D 596 (ASTM, 1983) suggests an acceptable ion percent difference of ±5% for samples containing 25 mg/L total dissolved solids.

Figure 1 summarizes the ion percent differences calculated from samples collected as a part of the National Atmospheric Deposition Program (NADP)/ National Trends Network (NTN) during 1984. The formula used to calculate the ion percent difference data was identical to that shown in the second column of Table 1. The histogram represents over 5000 weekly samples collected throughout the United States. These data are provided to indicate the range of values that are characteristic of wet deposition samples and to aid researchers in the development of their own reanalysis criteria. The ion percent difference data closely approximate a normal distribution with the mean value at less than 1% and a standard deviation (s) of approximately 7.5%. The normality of this distribution, with a mean value near zero percent, suggests that the use of warning and control limits of $\overline{x} \pm 2s$ and $\overline{x} \pm 3s$, respectively, would be appropriate. Using this approach, samples with ion percent differences greater than ±23% (3s) would be selected for chemical reanalysis. This procedure can also be used on a site specific basis after sufficient data have been collected to calculate a mean and standard deviation of the ion percent difference for each collection site.

Specific conductance data can also be used as a quality assurance check to verify the accuracy of analytical measurements. A calculated specific conductance can be determined by multiplying the ion concentrations by their equivalent conductance factors and summing the individual ion contributions (Topol et al., 1985). If the major ions in a precipitation sample have been analyzed, the calculated and measured specific conductance values should agree. A specific conductance percent difference calculation is made in an analogous manner to the ion percent difference calculation:

$$\text{Conductance percent difference} = \frac{\text{Calculated - Measured Conductance}}{\text{Measured Conductance}} \times 100$$

The conductance percent difference data can be used to develop a second set of criteria for the selection of samples for chemical reanalysis. The approach used by Peden (1983) for samples collected from the NADP/NTN monitoring network uses a three level rejection criteria based on the magnitude of the measured specific conductance combined with the calculated percentage difference (Table 3). Figure 2 represents a conductance percent difference histogram from the same 1984 NADP/NTN data set. Assuming that the measured concentration values that were used to generate these data are correct, the negative mean percent difference of 8.8% with a standard deviation (s) of 9.5% is an indication that all of the ions that contribute to the sample specific conductance have not been determined. Trace metals, fluoride, bromide, and organic acid anions are not routinely measured as a part of this monitoring network although they would be included as a component of the measured conductance. Conductance percent difference values tabulated from the Utility Acid Precipitation Study Program (UAPSP) (Electric Power Research Institute, 1983) indicated a median conductance difference of -0.8% with greater variability at low specific conductivities. Positive conductance percent differences ($\geq$10%) are an indication that one or more of the concentration values used in the calculation are suspect.

The histogram presented in Figure 2 does not approximate a normal distribution, but is negatively skewed. The use of statistical control limits is not a valid diagnostic tool under these conditions. These data can be used, however, as a guide in the development of laboratory specific reanalysis criteria. When combined with ion balance data, conductance verification procedures provide the necessary information to monitor the overall performance of laboratory analyses.

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Table 1. Comparison of Ion Balance Calculation Methods

Ion Percent Difference		Ion Ratio	
-200	100		0.00
-180	90	19.00	0.05
-160	80	9.00	0.11
-140	70	5.67	0.18
-120	60	4.00	0.25
-100	50	3.00	0.33
-80	40	2.33	0.43
-60	30	1.86	0.54
-40	20	1.50	0.67
-20	10	1.22	0.82
0	0	1.00	1.00
20	-10	0.82	1.22
40	-20	0.67	1.50
60	-30	0.54	1.86
80	-40	0.43	2.33
100	-50	0.33	3.00
120	-60	0.25	4.00
140	-70	0.18	5.67
160	-80	0.11	9.00
180	-90	0.05	19.00
200	-100	0.00	
$100 \times \frac{(\text{Cation}-\text{Anion})}{0.5(\text{Cation}+\text{Anion})}$	$100 \times \frac{(\text{Anion}-\text{Cation})}{(\text{Anion}+\text{Cation})}$	$\frac{\text{Anion}}{\text{Cation}}$	$\frac{\text{Cation}}{\text{Anion}}$

Table 2. Chemical Reanalysis Criteria Using Ion Percent Difference Data (from Peden, 1983)

If Anions + Cations (ueq/L) Are:	**And Ion Percent Difference[a] Is:**
<50	>±60
≥50<100	>±30
>100	>±15

a. Ion Percent Difference = $100 \times \dfrac{\text{Anion - Cation (ueq/L)}}{\text{Anion + Cation (ueq/L)}}$

Table 3. Chemical Reanalysis Criteria Using Conductance Percent Difference Data (from Peden, 1983)

If Measured Conductance (uS/cm) Is:	**And Conductance % Difference[a] Is:**
<5	>50
≥5<30	>30
≥30	>20

a. Conductance percent difference = $\dfrac{\text{Calculated - Measured Conductance}}{\text{Measured Conductance}} \times 100$

Figure 1. Ion Percent Difference Histogram for 1984 NADP/NTN Wet Side Samples.

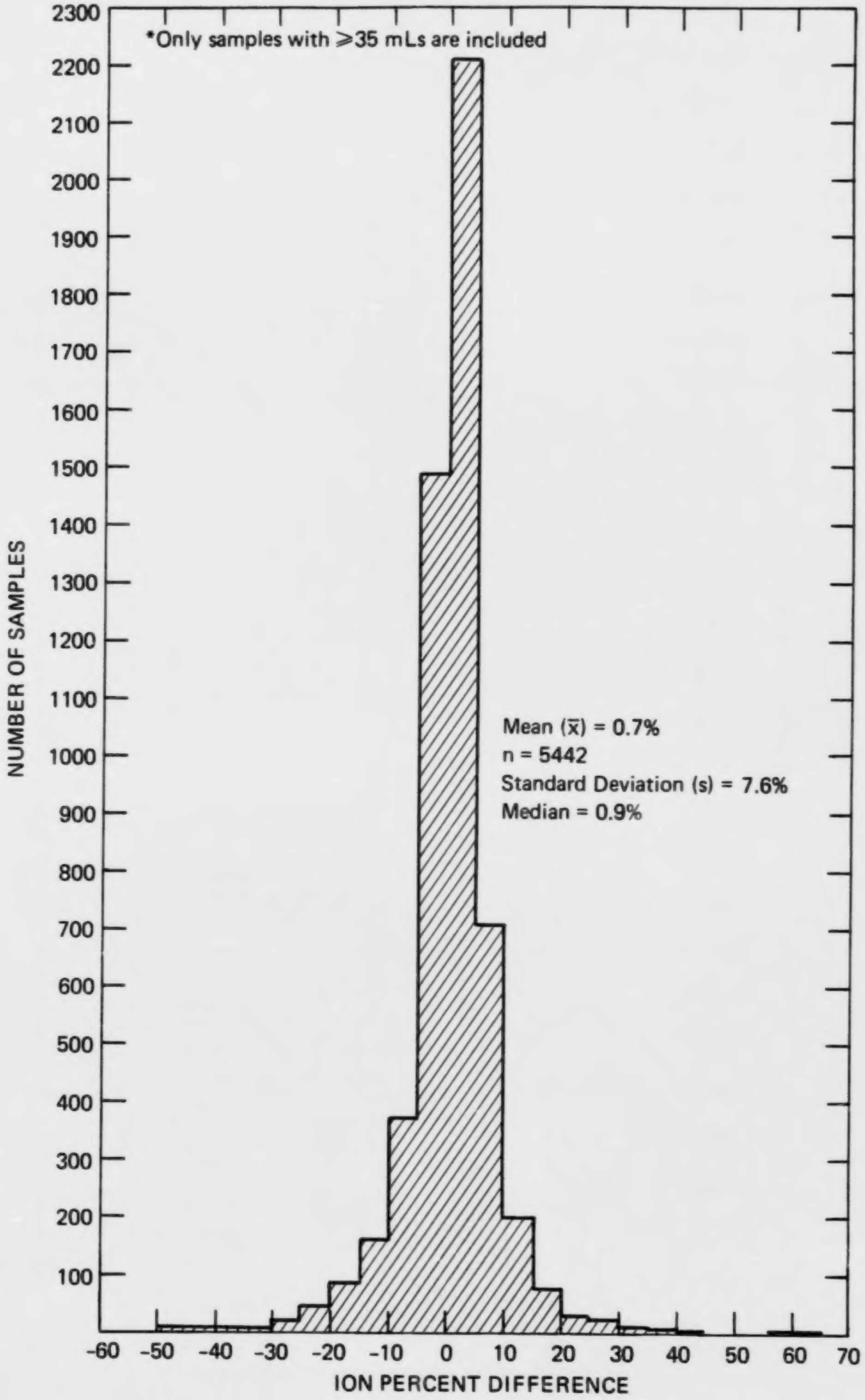
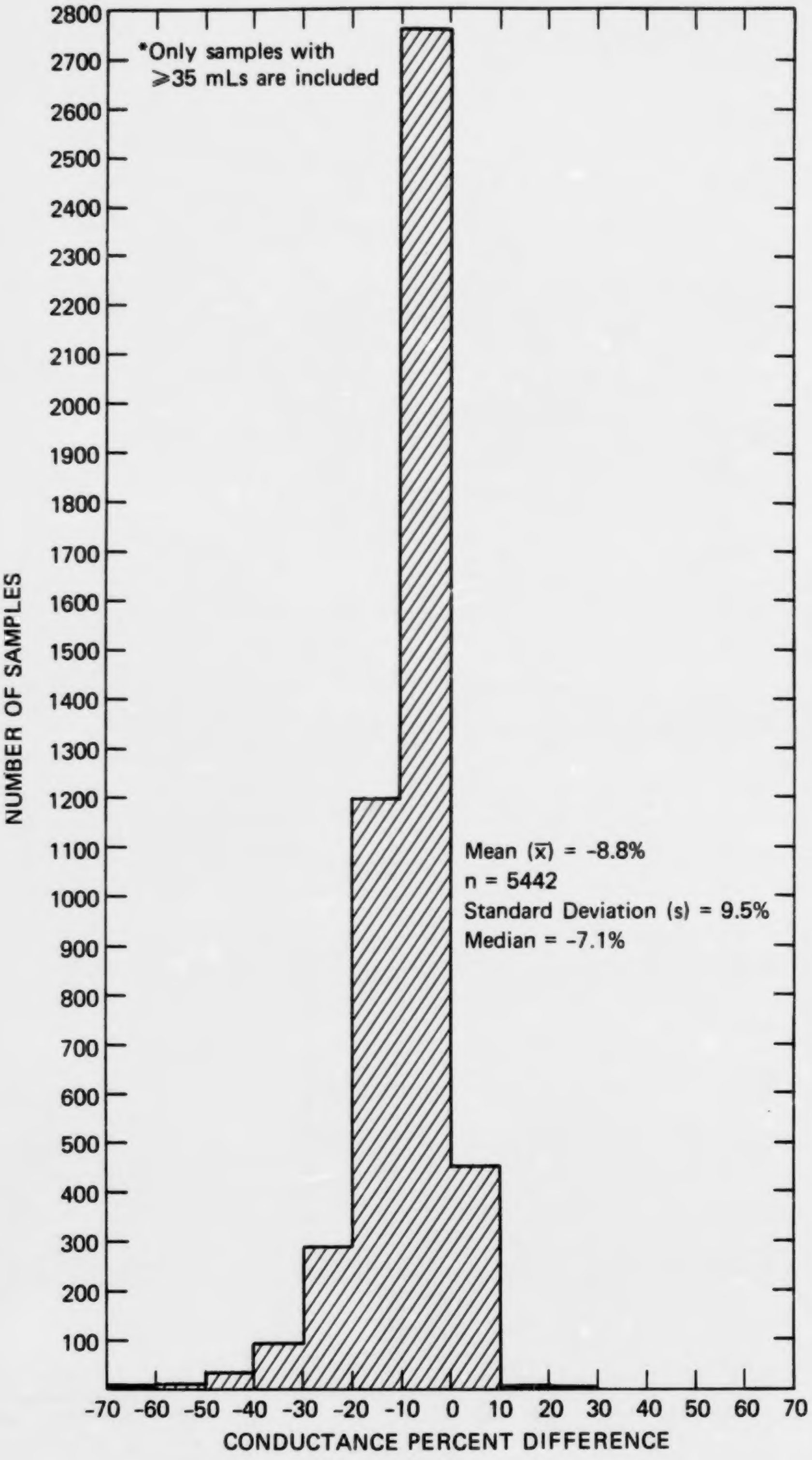


Figure 2. Conductance Percent Difference Histogram for 1984 NADP/NTN Wet Side Samples.



METHODS SUMMARY

The methods selected for inclusion in this manual represent the major inorganic ions common to wet deposition samples. Most of the instrumental procedures described are now being used by laboratories engaged in precipitation chemistry research. Detailed descriptions of test procedures with documentation of method detection limits, bias, and precision have not previously been available. As a result, data obtained from different laboratories reflected significant variations in bias, precision, reporting units, and quality control information. The purpose of this analytical methods manual is to provide the analytical chemistry community with standardized test procedures for the analysis of wet deposition samples. Specific quality control protocols that are necessary to generate high quality data are an integral part of the analytical methodologies.

Table 1 presents a percentile concentration summary of the eleven parameters measured in conjunction with the NADP/NTN precipitation chemistry network. These data, which include over 5000 weekly samples collected during 1984, were used extensively in the selection and evaluation of appropriate methodologies to include in this manual. The percentile concentrations were also used as a guide in the selection of spike recovery and quality control check sample concentrations. The suggested calibration standards and working concentration range for each method were selected to include at least 95% of the samples for each constituent. This selection of working ranges minimizes the need for sample dilutions while still providing precise measurements for the most dilute solutions.

The test methodologies include flame atomic absorption spectrophotometry, ion chromatography, automated colorimetry, titrimetry, and ion selective electrode procedures. In some cases, more than one method has been provided for a given analyte to provide alternative procedures if a specific type of instrumentation is not available. A comparison of detection limits, concentration ranges, bias, and precision for each analyte with two or more methodologies is presented in Table 2. These data are included as an aid in the selection of appropriate test procedures. For additional information on chemical interferences, analysis time, and sample volume requirements, refer to the detailed methods descriptions.

Table 1. Percentile Concentration Values of Chemical and Physical Parameters Measured In Wet Deposition

Parameter	**Min.**	**5th**	**10th**	**25th**	**50th**	**75th**	**90th**	**95th**	**Max.**
Ca (mg/L)	<0.009	0.030	0.050	0.080	0.170	0.380	0.760	1.20	22.80
Mg (mg/L)	<0.003	0.013	0.016	0.026	0.047	0.094	0.201	0.296	2.29
K (mg/L)	<0.003	0.008	0.010	0.017	0.030	0.061	0.125	0.186	5.81
Na (mg/L)	<0.003	0.027	0.035	0.059	0.118	0.269	0.625	1.05	10.80
NH_4 (mg/L)	<0.02	<0.02	<0.02	0.08	0.19	0.40	0.69	0.95	3.45
NO_3 (mg/L)	<0.02	0.15	0.27	0.58	1.13	1.99	3.13	4.11	27.35
Cl (mg/L)	<0.02	0.06	0.08	0.11	0.19	0.39	0.93	1.63	37.81
SO_4 (mg/L)	<0.10	0.39	0.50	0.83	1.49	2.65	4.27	5.68	45.72
PO_4 (mg/L)	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	0.006	0.009	12.60
pH (pH units)	2.98	4.01	4.15	4.38	4.80	5.46	6.08	6.34	7.85
Conductance (uS/cm)	1.6	3.7	5.0	8.5	15.2	26.9	42.4	54.2	566.8

Source: 1984 National Atmospheric Deposition Program (NADP)/ National Trends Network (NTN)

Number of samples (n) = 5450

Table 2. Comparison of Method Detection Limits, Bias, and Precision for Flame Atomic Absorption Spectrophotometry (FAAS), Ion Chromatography (IC), Automated Colorimetry (AC), and Ion Selective Electrode (ISE).

Analyte	Method	Method Detection Limit, mg/L	Concentration Range, mg/L	Theoretical Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
Ammonium	IC[b]	0.03	0.03 - 1.00	0.063	7	0.004	6.4	0.011	16.4
				0.400	7	0.000	0.0	0.032	8.0
	AC	0.03	0.03 - 2.00	0.19	215	-0.01	-5.3	0.02	11.1
				0.36	82	0.00	0.0	0.02	5.6
				0.98	224	-0.06	-6.1	0.05	5.4
				1.22	81	0.02	1.6	0.03	2.4
	ISE	0.05	0.05 - 2.00	0.18	12	-0.01	-5.6	0.02	10.6
				0.39	12	-0.01	-2.6	0.02	6.6
Calcium	FAAS	0.007	0.007 - 3.00	0.053	145	-0.002	-3.8	0.002	3.9
				0.406	145	0.007	1.7	0.003	0.7
	IC[b]	0.02	0.02 - 3.00	0.053	7	0.005	9.4	0.006	10.3
				0.406	7	-0.001	-0.2	0.045	11.1
Chloride	IC	0.03	0.03 - 2.00	0.18	132	0.01	5.6	0.02	10.5
				0.85	479	0.02	2.4	0.03	3.4
				1.78	255	0.10	5.6	0.05	2.7
	AC	0.03	0.03 - 2.00	0.85	105	0.03	3.5	0.02	2.3
				1.78	105	0.09	5.1	0.03	1.6

Table 2. (continued)

Analyte	Method	Method Detection Limit, mg/L	Concentration Range, mg/L	Theoretical Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
Magnesium	FAAS	0.002	0.002 - 1.00	0.018	145	-0.001	-5.6	0.001	5.9
				0.084	145	-0.001	-1.2	0.001	1.2
	IC[b]	0.02	0.02 - 1.00	0.018	7	0.008	44.4	0.008	30.8
				0.084	7	0.001	1.2	0.018	21.2
Nitrate	IC	0.03	0.03 - 5.00	0.80	485	0.01	1.2	0.02	2.5
				3.54	415	0.10	2.8	0.12	3.3
Nitrate-Nitrite	AC	0.02	0.02 - 5.00	0.62	88	0.01	1.6	0.02	3.2
				0.80	24	-0.02	-2.5	0.01	1.3
				3.17	88	-0.06	-1.9	0.07	2.2
				3.54	23	-0.10	-2.8	0.05	1.4
Orthophosphate	IC	0.02	0.02 - 0.25	0.05	10	0.00	0.0	0.00	0.0
				0.15	10	0.00	0.0	0.01	6.7
	AC[b]	0.02	0.02 - 0.25	0.031	151	-0.005	-16.1	0.007	26.9
				0.062	161	-0.007	-11.3	0.008	14.5
				0.123	84	-0.006	-4.9	0.006	5.1
				0.215	74	-0.010	-4.6	0.010	4.9

Table 2. (continued)

Analyte	Method	Method Detection Limit, mg/L	Concentration Range, mg/L	Theoretical Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
Potassium	FAAS	0.003	0.003 - 1.00	0.021	127	-0.001	-4.8	0.001	5.0
				0.098	122	-0.003	-3.1	0.001	1.0
	IC[b]	0.01	0.01 - 1.00	0.021	7	0.003	14.3	0.004	16.7
				0.098	7	0.000	0.0	0.005	5.1
Sodium	FAAS[c]	0.003	0.003 - 1.00	0.082	123	0.002	2.4	0.001	1.2
				0.465	122	0.014	3.0	0.003	0.6
	IC[b]	0.03	0.03 - 1.00	0.082	7	0.008	9.8	0.009	10.0
				0.465	7	-0.011	-2.4	0.019	4.2
Sulfate	IC	0.03	0.03 - 8.00	0.72	340	0.00	0.0	0.03	4.2
				0.94	482	-0.02	-2.1	0.03	3.3
				3.60	122	0.09	2.5	0.11	3.0
	AC	0.05	0.05 - 6.00	0.94	170	-0.04	-4.2	0.06	6.7
				7.20	172	-0.07	-1.0	0.11	1.5

A portion of the above data was obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

a. Number of replicates
b. Concentrations are significant to two decimal places
c. 589.0 nm wavelength setting

Method 120.6 -- Specific Conductance in Wet Deposition by Electrolytic Determination

March 1986

Performing Laboratory:

Carla Jo Brennan
Jackie Sauer
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Single-Operator Bias and Precision for Specific Conductance Measurements Determined from Quality Control Check Samples.
2. Specific Conductance of KCl Solutions at 25°C as a Function of the Molar Concentration.

FIGURES

1. Percentile Conductance Values Obtained from Wet Deposition Samples.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of specific conductance in wet deposition samples by electrolytic measurement using a conductance cell as the sensor.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 Figure 1 represents a cumulative frequency percentile specific conductance plot obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of calibration standards. The operating range of this method is 0.10-1000 uS/cm. Most wet deposition samples have a specific conductance in the range of 5 to 50 uS/cm.

2. SUMMARY OF METHOD

2.1 Specific conductance is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, mobility, and valence. Conductance is also a function of the relative concentrations of the ions in solution and of the solution temperature. The physical measurement made in a laboratory determination of specific conductance is resistance, expressed as:

$$R = K\ (l/a)$$

where: a = cross section of conductor (cm^2)
l = length of conductor (cm)
$K = \text{cell constant} = \dfrac{\text{Measured Resistance}}{\text{Specific Resistance}}$

Specific resistance is the resistance of a cube 1 cm on an edge. Since commercially available conductance cells measure a given fraction of the specific resistance, it is necessary to include the cell constant when determining specific conductance. The conductance meter and the associated cell are calibrated using potassium chloride solutions of known specific conductances comparable to that found in wet deposition samples.

3. DEFINITIONS

3.1 ELECTRICAL CONDUCTANCE -- the reciprocal of the resistance in ohms measured between opposite faces of a centimeter cube of an aqueous solution at a specified temperature (14.1).

3.2 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 The conductance cell reliably measures specific conductance in nearly all aqueous solutions and in general is not subject to solution interferences from color, turbidity, oxidants, or reductants.

4.2 Exposure of samples to laboratory atmosphere can result in the absorption of carbon dioxide, ammonia, and other gases by the solution being analyzed. With this absorption of additional electrolytes, the measured conductance of the sample is elevated. To minimize errors, keep all sample aliquots tightly covered prior to analysis.

4.3 Organic materials dispersed in water will affect the cell constant and the accuracy of measurements by coating the electrode surface. To remove these coatings, refer to the manual accompanying the conductance cell for the manufacturer's recommendations for cleaning the cell.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated nitric acid (Sect. 7.4).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.3).

6. APPARATUS AND EQUIPMENT

6.1 SPECIFIC CONDUCTANCE METER -- Select an instrument equipped with a manual or electrically balanced conductance bridge, powered by battery or 110 V AC line. If battery powered, however, the meter must have a battery check feature. Select an instrument capable of measuring conductance with an error not exceeding 1% or 1 uS/cm, whichever is greater. The meter used must have a range of 0.1-1000 uS/cm and readability to 0.1 uS/cm sensitivity.

6.1.1 Check the electronic calibration of the meter monthly and adjust when necessary. This may be accomplished either through use of an internal calibration feature or an external calibration set.

6.3 SPECIFIC CONDUCTANCE CELL -- Conductance cells are available in pipette, flow-through, cup, or immersion form. Select a cell having a constant of 1.0 or 0.1. A sample volume requirement of 10 mL or less is desirable.

6.3.1 When not in use, rinse the cell thoroughly with water (Sect. 7.2) and store according to manufacturer's guidelines.

6.3.2 If readings become erratic, refer to the manual accompanying the cell for the manufacturer's recommendations.

6.4 THERMOMETER -- Select a thermometer capable of being read to the nearest 0.1°C and covering the range 0°-40°C.

6.5 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room. Maintain laboratory temperature within ±3°C.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.4). Point of use 0.2 micrometer filters are recommended for all faucets supplying ASTM Type II water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 POTASSIUM CHLORIDE REFERENCE SOLUTION (5.0×10^{-4} N) -- Dissolve 37.28 mg anhydrous potassium chloride (KCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L. This solution has a specific conductance of 73.9 uS/cm at 25°C. Store the reference solution at room temperature in a tightly sealed high density polyethylene or polypropylene container for a period not exceeding one year.

7.3.1 Determine if the meter reading is linear throughout all range settings using the reference solution described above. If not, recalibrate the meter at higher and/or lower settings as needed with different concentrations of KCl reference solution prepared according to Table 2.

7.4 QUALITY CONTROL CHECK SAMPLE (5.0×10^{-5} N HNO_3) -- Dilute 1.0 mL of concentrated nitric acid (HNO_3, sp gr 1.42) to 1 L with water (Sect. 7.2). Dilute 3.2 mL of this stock solution to 1 L with water. The resulting solution has a conductance of 21.8 uS/cm at 25°C. Store at room temperature in a high density polyethylene or polypropylene container for a period not exceeding one year.

7.5 SAMPLE CONTAINERS -- Use glass or disposable polyolefin sample cups if the conductance cell selected requires a sample container. Rinse the sample cups a minimum of three times with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants. Air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from sequential sampling within a wet deposition event to weekly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The dissolution of particulate materials and the presence of microbial activity will affect the stability of the ions in wet deposition samples (14.5). This instability can result in either an increase or a decrease in specific conductance of the solution. Measurements of conductance should be made immediately after sample collection and thermal equilibration with calibration standard(s). Refrigeration of samples at 4°C will minimize but not prevent changes in specific conductance.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is effective at stabilizing changes in conductance that result from the dissolution of alkaline particulate matter (14.5). Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus.

9. CALIBRATION AND STANDARDIZATION

9.1 Bring all standards and samples to ambient temperature, ($\pm 1^{\circ}C$).

9.2 Rinse the specific conductance cell at least three times with the same volume of KCl standard as the aliquot to be measured. Measure the conductance of a fourth portion of the KCl standard. The conductance measured for the calibration solution must agree within ±2 uS/cm of the nominal value.

9.3 CELL CONSTANT

9.3.1 If the meter selected requires that a cell constant be calculated, use the equations provided in Sect. 12.2.

9.3.2 If the specific conductance of the reference solution is incorporated into the meter for direct readout of conductance, follow the manufacturer's guidelines for calibration.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.6). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor the analyses of quality control check samples (QCS).

10.2.1 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) for the measured conductance of each QCS solution. Use the certified or NBS traceable specific conductance as the mean (target) value ($\bar{x}$) for determining control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. If the measured conductance for the QCS solutions fall outside of the $\pm 3s$

limits, recalibrate the system and reanalyze all samples from the last time the system was in control. If two successive QCS conductance measurements are outside of the ±2s limits, verify the meter calibration according to Sect. 10.5 before continuing with sample measurements. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 1. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.2 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the specific conductance of the solution. If the measured conductance is greater than 3 uS/cm, a contamination problem is indicated in the cleaning procedure. Corrective action should be taken before the sampling containers are used for the collection of wet deposition.

10.4 Conductance cells used for the measurement of wet deposition samples should not be used for other sample types. Strongly acidic or basic solutions may cause cell degradation and result in biased measurements. Similarly, samples characterized by high concentrations of organic matter may leave a residue on the cell resulting in inaccurate measurements.

10.5 Verify the meter calibration after every ten samples and at the end of each day's analyses. If the measured conductance falls outside of the limits described in Sect. 9.2, recalibrate the conductance meter assembly and reanalyze those samples analyzed since the last calibration.

10.6 Determine the conductance of a quality control check sample (QCS) after the meter and cell assembly have been calibrated. This sample may be formulated in the laboratory, obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater), or the United States Environmental Protection Agency (NBS Traceable Reference Material). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample selected should approximate the conductance of the samples to be analyzed. If the measured value for the QCS is not within the specified limits of the control solution, measure a second aliquot. Failure to obtain acceptable results on the second aliquot indicates a problem with the cell or meter. Check the conductance meter according to the manufacturer's guidelines. If a cell problem is indicated, replace the cell and repeat the calibration procedure before measuring the QCS again. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.6.1 The conductance of the QCS should be measured after every ten samples or after completion of a batch of samples consisting of less than ten. If the QCS measurement is out of the predetermined control limits, check the calibration and recalibrate if it has shifted by more than 2 uS/cm. Recheck the QCS and reanalyze all samples from the last time the measurement system was in control.

10.7 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Determine the temperature of the wet deposition sample to be tested and bring all standards and samples to ambient temperature, (±1°C).

11.2 Calibrate the conductance assembly as described in Sect. 9.

11.3 After the cell and meter are calibrated, measure the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.1), refer to Sect. 10.6.

11.4 Rinse the cell at least three times with the same volume of water (Sect. 7.2) as the sample aliquot to be measured, discarding each rinse. Determine the specific conductance of a fourth portion of the water to the nearest 0.1 uS/cm. If the corrected specific conductance exceeds 1.0 uS/cm, the water is not suitable for use in specific conductance measurements. Discard the water and any standard solutions or quality control check samples that have been prepared using that water.

11.5 Rinse the cell at least three times with the same volume of water (Sect. 7.2) as the sample aliquot to be measured, discarding each rinse. Rinse the cell with an aliquot of the wet deposition sample to be measured. Discard the rinse solution. Determine the specific conductance of a second portion of the sample.

Note: When the same sample aliquot must be used for further analyses, measure the specific conductance prior to all other determinations. Measurement of pH especially must be postponed. Leakage of reference solution from a pH reference cell will alter the measured value of the specific conductance of the solution (14.7).

12. CALCULATIONS

12.1 If the meter selected has a feature that allows adjustment of the direct readout of the specific conductance standard to the theoretical value, no calculations are required.

12.2 CELL CONSTANT -- If the meter selected requires that a cell constant be calculated, follow the instructions provided below:

12.2.1 Compute the corrected cell constant, K_C, that includes the calculation for the cell constant, K, and temperature correction to 25°C, using the conductance value obtained in Sect. 9.2 and the following equation:

$$K_C = \frac{74 \text{ uS/cm}}{KCl_M}$$

where: KCl_M = conductance value measured for the KCl standard (uS/cm)

12.2.2 Determine the corrected specific conductance for the water (Sect. 7.2) using the corrected cell constant, the conductance value measured in Sect. 11.4, and the following equation:

$$W_C = K_C \times W_M$$

where: W_C = Corrected specific conductance value for the water sample (uS/cm)

W_M = Specific conductance value measured for the water sample (uS/cm)

12.2.3 Determine the corrected sample conductance using the following equation, the corrected cell constant, and the conductance value measured in Sect. 11.5.

$$S_C = K_C \times S_M$$

where: S_C = Corrected specific conductance value for the wet deposition sample (uS/cm)
S_M = Specific conductance value measured for the wet deposition sample (uS/cm)

12.3 Report specific conductance to the nearest tenth in units of uS/cm.

13. PRECISION AND BIAS

13.1 Single operator precision and bias were determined from measurements of quality control check samples that approximated the conductance range of wet deposition samples. The results are tabulated in Table 1.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Definitions of Terms Related to Water," Standard D 1129-82b, 1982, p. 4.

14.2 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.3 "Safety in Academic Chemical Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.4 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.5 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. **12**, 1978, pp. 2343-2349.

14.6 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985 U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.7 Koch, W. G., Marinenko, G., and Stolz, J. W., "Simulated Precipitation Reference Materials, IV," National Bureau of Standards (U.S.), NBSIR 82-2581, June 1982, p. 3.

Table 1. Single-Operator Bias and Precision of Specific Conductance Measurements Determined from Quality Control Check Samples.

Theoretical Conductance, uS/cm	Mean Measured Conductance, uS/cm	n[a]	Bias, uS/cm	Bias, %	Precision s, uS/cm	Precision RSD, %
21.8	22.0	80	0.2	1.0	0.3	1.4
128.0	128.2	9	0.2	0.1	2.0	1.6

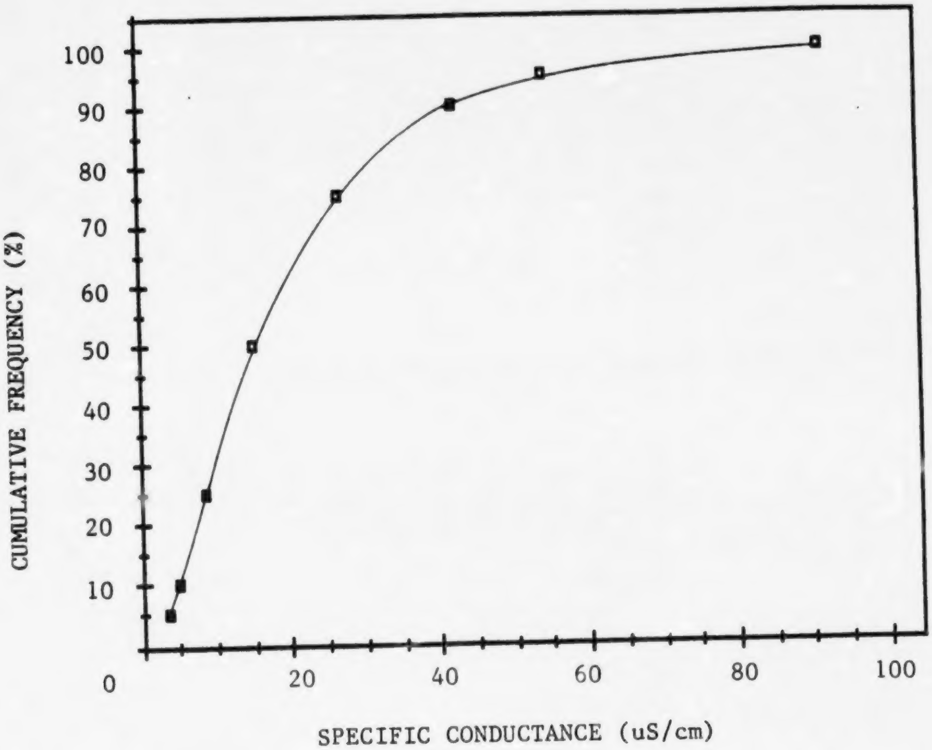
The above data were obtained from the records of conductance measurements made under the direction of the NADP quality assurance program. The quality control solutions used were a 5.01×10^{-5}N nitric acid solution having a calculated specific conductance of 21.8 uS/cm at 25°C and a simulated rainwater solution (Research Material #8409-II) provided by the National Bureau of Standards.

[a] Number of replicates.

Table 2. Specific Conductance of KCl Solutions at 25°C as a Function of the Molar Concentration.

Concentration, moles of KCl/L	Specific Conductance, uS/cm
0.0001	14.89
0.0002	29.71
0.0003	44.47
0.0004	59.20
0.0005	73.89
0.0006	88.55
0.0007	103.19
0.0008	117.80
0.0009	132.38
0.0010	146.95

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Specific Conductance



Method 150.6 -- pH of Wet Deposition by Electrometric Determination

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Performing Laboratory:

Jackie Sauer
Jacqueline M. Lockard
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Values for F/(2.3026 RT) at Different Temperatures.
2. Suitable pH Reference Electrodes for the Analysis of Wet Deposition Samples.
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1. Percentile pH Values Obtained from Wet Deposition Samples.
2. Time Required to Obtain Stable pH Response in Wet Deposition Samples.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of pH in wet deposition samples by electrometric measurement using either a pH half cell with a reference probe or a combination electrode as the sensor.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 Figure 1 represents a cumulative frequency percentile pH plot obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration buffers.

2. SUMMARY OF METHOD

2.1 Electrodes approximate the pH of a solution by the Nernst equation that relates the potential measured by the pH electrode in a standard buffer solution to that measured in an unknown sample:

$$pH = pH_s + \frac{(E - E_s)F}{2.3026\ RT}$$

where: pH_s = pH of the standard buffer solution
E = potential measured in an unknown sample
E_s = potential measured in the buffer solution
F = Faraday's constant
R = gas constant
T = absolute temperature $(T(^{\circ}C) + 273)$

Values of the factor F/(2.3026 RT) at different temperatures are provided in Table 1. The pH meter and the associated electrode(s) are calibrated with two reference buffer solutions that bracket the anticipated sample pH. The pH of the wet deposition sample is determined from this calibration.

3. DEFINITIONS

3.1 pH -- the negative logarithm to the base ten of the conventional hydrogen ion activity (14.1):

$$pH = -\log[H^+]$$

3.2 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 The pH meter and the associated electrode(s) reliably measure pH in nearly all aqueous solutions and in general are not subject to solution interferences from color, turbidity, oxidants, or reductants.

4.2 The true pH of an aqueous solution is affected by the temperature. The electromotive force between the glass and the reference electrode is a function of temperature as well as pH. Temperature effects caused by a change in electrode output can be compensated for automatically or manually depending on the pH meter selected.

4.3 Organic materials dispersed in water appear to poison the glass electrode, particularly when analyzing low ionic strength solutions. Difficulty encountered when standardizing the electrode(s), erratic readings, or slow response times may be an indication of contamination of the glass bulb. To remove these coatings, refer to the manual accompanying the probe for the manufacturer's recommendations.

4.4 When analyzing samples that have low ionic strengths, such as wet deposition, an effect known as "residual junction potential" can lead to errors as large as 0.1 pH units (14.3). This error occurs when the junction potential of the sample differs greatly from that of the standard. These conditions are frequently met in wet deposition analyses when the pH electrode(s) is calibrated with high ionic strength standard reference buffers. This error is reduced by using a reference electrode with a ceramic junction.

4.5 When measuring the pH of wet deposition, the sample may be agitated to speed electrode response. Care must be taken, however, to avoid introducing a source of error known as "residual streaming potential" that can result in a significant difference between the stirred and unstirred pH of the sample (14.4). The magnitude of the streaming potential is dependent on the electrode(s) and on the stirring rate. Differences in pH for stirred and unstirred wet deposition samples when the electrode assembly has been calibrated only with quiescent reference standards average 0.05 pH units at a stirring rate of 4 revolutions per second.

4.5.1 Eliminate the errors associated with residual streaming potentials by agitating all calibration standards and wet deposition samples thoroughly to speed electrode response and then allowing each aliquot to become quiescent before taking a pH reading.

4.5.2 If magnetic stirring is used, take care not to contaminate the sample when inserting the stirring bar. Maintain an air space between the surface of the stirring motor and the sample container to prevent heating the wet deposition sample.

5. SAFETY

5.1 The reference buffer solutions, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated nitric (Sect. 7.4) and hydrochloric acids (Sect. 7.5.1) and sodium hydroxide (Sect. 7.5.3-7.5.4).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.5).

6. APPARATUS AND EQUIPMENT

6.1 LABORATORY pH METER -- The meter may have either an analog or digital display with a readability of 0.01 pH units. A meter that has separate calibration and slope adjustment features and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be powered by battery or 110 V AC line; if battery powered, the meter must have a battery check feature. A temperature compensator control to allow accurate measurements at temperatures other than 25°C is desirable.

6.2 SENSING ELECTRODE -- Select a sensing electrode constructed of general purpose glass. This electrode type is characterized by low resistance, quick response, and has a reliable range of 0-14 pH units. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

6.3 REFERENCE ELECTRODE -- The reference electrode recommended for wet deposition analysis is one equipped with a ceramic junction. The ceramic construction minimizes differences in potential between high ionic strength buffers and low ionic strength samples thus reducing errors from residual junction potential (14.3). A reference probe equipped with a ceramic junction in an annular ring configuration generates a more stable potential in less time due to a higher flow of internal electrolyte into the solution. Single pore ceramic frit junctions also provide adequate electrolyte flow. Table 2 lists suitable reference electrodes that have been found to be satisfactory. Other electrodes having similar characteristics are also suitable. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

6.4 COMBINATION ELECTRODE -- The combination electrode combines the indicating and reference elements in a single unit. Since sample volume requirements are a consideration when analyzing wet deposition samples, combination electrodes are more convenient than separate glass and reference electrodes. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

6.5 TEMPERATURE CONTROL -- To ensure accurate results, use either a constant temperature water bath, a temperature compensator, or a thermometer to verify that all standards and samples are maintained at temperatures within ±1°C of one another. If a thermometer is used, select one capable of being read to the nearest 1°C and covering the range 0°-40°C.

6.6 STIRRING DEVICE (optional) -- electric or water-driven. If an electric stirrer is selected, leave an air gap or place an insulating pad between the stirrer surface and the solution container to minimize heating of the sample. Use a TFE-fluorocarbon-coated stirring bar.

6.7 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.6). Point of use 0.2 micrometer filters are recommended for all faucets supplying ASTM Type II water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 QUALITY CONTROL CHECK SAMPLE (QCS) (5.0×10^{-5} N HNO_3) -- Dilute 1.0 mL of concentrated nitric acid (HNO_3, sp gr 1.42) to 1 L with water (Sect 7.2). Dilute 3.2 mL of this stock solution to 1 L with water (Sect 7.2). The resulting solution has a pH of 4.30 ± 0.10 at 25°C. Store at room temperature in a high density polyethylene or polypropylene container. This solution is stable for one year.

7.4 REFERENCE BUFFER SOLUTIONS -- Table 3 identifies each buffer salt by its National Bureau of Standards (NBS) number and provides a recommended drying procedure prior to use. Store the reference buffer solutions in polyethylene or chemical-resistant glass bottles and replace after one year or sooner if a visible change such as the development of colloidal or particulate materials is observed.

7.4.1 Phthalate Reference Buffer Solution (0.02 N HCl, 0.05 N $KHC_8H_4O_4$) -- Add 83.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to water (Sect. 7.2) and dilute to 1 L. Dissolve 10.20 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in 22.3 mL of the hydrochloric acid solution and dilute to 1 L with water (Sect. 7.2). This solution has a pH of 3.00 at 25°C.

7.4.2 Phthalate Reference Buffer Solution (0.05 N $KHC_8H_4O_4$) -- Dissolve 10.12 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water (Sect. 7.2) and dilute to 1 L. This solution has a pH of 4.00 at 25°C.

7.4.3 Phosphate Reference Buffer Solution (0.005 N NaOH, 0.05 N KH_2PO_4) -- Dissolve 4.00 g of sodium hydroxide (NaOH) in water (Sect. 7.2) and dilute to 1 L. Dissolve 6.80 g of potassium dihydrogen phosphate (KH_2PO_4) in 56.0 mL of the hydroxide solution and dilute to 1 L with water (Sect. 7.2). This solution has a pH of 6.00 at 25°C.

7.4.4 Phosphate Reference Buffer Solution (0.03 N NaOH, 0.05 N KH_2PO_4) -- Dissolve 40.0 g of sodium hydroxide (NaOH) in water (Sect. 7.2) and dilute to 1 L. Dissolve 6.80 g of potassium dihydrogen phosphate (KH_2PO_4) in 29.1 mL of the hydroxide solution and dilute to 1 L with water (Sect. 7.2). This solution has a pH of 7.00 at 25°C.

7.4.5 Commercial Buffer Solutions -- Commercially available buffer solutions traceable to NBS buffers are adequate for standardization. These commercial buffer solutions usually have pH values near 3, 4, 6, and 7, the exact pH and use temperature being provided by the supplier of the specific buffer.

7.5 SAMPLE CONTAINERS -- Use glass or polyolefin sample cups that have been thoroughly rinsed with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with water (Sect. 7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants. Air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from sequential sampling within a wet deposition event to weekly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The dissolution of particulate materials and the presence of microbial activity will affect the stability of hydrogen ions (pH) in wet deposition samples (14.7, 14.8). This instability generally results in a decrease in hydrogen ions (higher pH). Measurements of pH should be made immediately after sample collection and thermal equilibration with calibration buffers. Refrigeration of samples at $4^\circ C$ will minimize but not prevent a decrease in the hydrogen ion content.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is effective at stabilizing pH values that are influenced by the dissolution of alkaline particulate matter (14.7). Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus.

8.3.2 A biocide such as chloroform ($CHCl_3$) may be used to stabilize the organic acid component of the measured pH and to prevent pH changes due to biological reactions on other sample constituents (14.8). Add the chloroform (0.5 mL per 250 mL sample) to a separate sample aliquot that will be used only for the measurement of pH.

9. CALIBRATION AND STANDARDIZATION

9.1 Turn on the meter and allow it to warm up according to manufacturer's instructions.

9.2 If necessary, add filling solution to the electrode before using. Maintain the filling solution level at least one inch above the level of the sample surface to ensure proper electrolyte flow rate.

9.3 Determine the temperature of the wet deposition sample. Allow sample, buffers, and QCS solutions to reach room temperature before making pH measurements or bring the temperature of all solutions to within $\pm 1^\circ C$ of each other.

9.4 Select two reference buffer solutions that bracket the anticipated pH of the wet deposition sample. The difference between the nominal pH values of the two buffers should not exceed three pH units. Buffer solutions with pH's of 7.00 and 4.00 are recommended for wet deposition samples.

9.5 CALIBRATION FUNCTION

9.5.1 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Dispense two aliquots of the buffer with the higher pH into separate, clean sample cups. Insert the electrode(s) into one aliquot for 30 seconds.

9.5.2 Remove the electrode(s) from the first aliquot and insert directly into the second. Allow either two minutes for equilibration or allow sufficient time for the reading to remain steady within ±0.01 pH units for 30 seconds.

9.5.3 Adjust the calibration control until the reading corresponds to the temperature corrected value of the reference buffer solution.

9.6 SLOPE FUNCTION

9.6.1 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Dispense two aliquots of the second reference buffer solution into separate, clean sample cups. Insert the electrode(s) into one aliquot for 30 seconds.

9.6.2 Remove the electrode(s) from the first aliquot and insert directly into the second. Allow the system to equilibrate as directed in Sect. 9.5.2.

9.6.3 Adjust the slope function until the reading corresponds to the temperature corrected value of the reference buffer solution.

9.7 CALIBRATION CHECK

9.7.1 Remove the electrode(s), rinse thoroughly, and place into the first reference buffer solution. If the pH does not read within ±0.01 units of the temperature corrected value, repeat the calibration procedure until the buffers agree.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for precipitation measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.9). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor the analyses of quality control check samples (QCS).

10.2.1 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days to provide a realistic estimate of method variability. Calculate a standard deviation (s) for the pH measurements for each QCS solution. Use the certified or NBS traceable pH value as the mean (target) value ($\bar{x}$) for determining the control limits. A warning limit of ±2s and a control limit of ±3s should be used. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. If the pH measurements for the QCS solutions fall outside of the ±3s limits, recalibrate the system and reanalyze all samples from the last time the system was in control. If two successive QCS pH measurements are outside of the ±2s limits, verify the meter calibration according to Sect. 10.5 before continuing with sample measurements. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 4. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.2 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the solution pH. If the measured pH is not within the range of 5.4-6.0, a contamination problem is indicated in the cleaning procedure. Corrective action should be taken before the sampling containers are used for the collection of wet deposition.

10.4 Electrodes used for the measurement of wet deposition samples should not be used for other sample types. Strongly acidic or basic solutions may cause electrode degradation and result in biased measurements and/or slow response in precipitation samples. Similarly, samples characterized by high concentrations of organic matter may leave a residue on the glass sensing bulb resulting in slow electrode response.

10.5 Verify the meter calibration after every ten samples and at the end of each day's analyses using both reference buffer solutions. The pH measured for the calibration buffers must agree within ±0.02 of the temperature corrected value reported for each buffer. If the measured pH of either buffer falls outside of these limits, recalibrate the electrode/meter assembly and reanalyze those samples analyzed since the last time the system was in control.

10.6 Determine the pH of a quality control check sample (QCS) after the meter and electrode assembly have been calibrated. This sample may be formulated in the laboratory, obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater), or the United States Environmental Protection Agency (NBS Traceable Reference Material). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample selected must be within the range of the calibration buffers and should approximate the pH range of the samples to be analyzed. If the measured value for the QCS is not within the specified limits of the control solution, measure a second aliquot. Failure to obtain acceptable results on the second aliquot indicates a problem with the electrode or meter. Check the pH meter according to the manufacturer's guidelines. If an electrode problem is indicated, replace the electrode and repeat the calibration procedure before measuring the QCS again. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision

10.6.1 QCS measurements should be made after every ten samples or after completion of a batch of samples consisting of less than ten. If the QCS measurement is out of the predetermined control limits, check the calibration buffers and recalibrate if any one of the buffer values has shifted by more than 0.02 pH units. Recheck the QCS and reanalyze all samples from the last time the measurement system was in control.

10.7 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.8 Participation in performance evaluation studies is recommended for precipitation chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for precipitation chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Bring all buffers, solutions, and samples to ambient temperature making sure any necessary compensation is made for deviations in temperature (Sect. 6.5).

11.2 Calibrate the electrode assembly with two reference buffer solutions as described in Sect. 9.1-9.7.

11.3 After the electrode(s) and meter are calibrated, analyze a QCS sample. If the measured value for the QCS is not within the specified limits (Sect. 10.2.1), refer to Sect. 10.6.

11.4 SAMPLE ANALYSIS

11.4.1 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Dispense two aliquots of wet deposition sample into separate, clean sample cups. Insert the electrode(s) into one aliquot for 30 seconds.

11.4.2 Remove the electrode(s) from the first aliquot and insert directly into the second, once again allowing the system time to stabilize. Record the pH measurements when readings differ by no more than ±0.01 pH units within a 30 second period. Record the pH and the temperature of the sample.

Note: The time necessary for the system response to stabilize depends on the pH of the sample. As Figure 2 illustrates, the pH electrode response time is usually three to five minutes for samples with a $pH \leq 5.5$. For samples with $pH > 5.5$, a stable response is usually generated in five to seven minutes.

12. CALCULATIONS

12.1 Most pH meters are calibrated in pH units and the pH of the sample is obtained directly by reading the meter scale. Record pH measurements to the nearest hundredth of a pH unit and sample temperature to the nearest degree.

13. PRECISION AND BIAS

13.1 Single-operator precision and bias data were obtained using three quality control check samples. The results are tabulated in Table 4.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Definitions of Terms Relating to Water," Standard D 1129-82b, 1982, p. 5.

14.2 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.3 Koch, W. G., Marinenko, G., and Stolz, J. W., "Simulated Precipitation Reference Materials, IV," National Bureau of Standards (U.S.), NBSIR 82-2581, June 1982, p. 14.

14.4 McQuaker, N. R., Kluckner, P. D., and Sandberg, D. K., "Chemical Analysis of Acid Precipitation: pH and Acidity Determinations," Environ. Sci. Technol., **Vol. 17**, No. 7, 1983, pp. 431-435.

14.5 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.6 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.7 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. **12**, 1978, p. 2343-2349.

14.8 Keene, W. C. and Galloway, J. N., "Organic Acidity in Precipitation of North America," Atmos. Environ. **18**, 1984, p. 2491-2497.

14.9 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

Table 1. Values for F/(2.3026 RT) at Different Temperatures.

Temperature, °C	F/(2.3026 RT), V^{-1}
0	18.4512
5	18.1195
10	17.7996
15	17.4907
20	17.1924
25	16.9041
30	16.6253
35	16.3555
40	16.0944
45	15.8414

The above data were calculated using a precise value of the logarithmic conversion factor (2.302585) and values of the fundamental constants.

F = 96,487.0 C/eq
R = 8.31433 J/K mol
T = 273.15 + °C

Table 2. Suitable pH Reference Electrodes for the Analysis of Wet Deposition Samples.

Manufacturer	Model Number	Electrode Type
Beckman	39417	glass bodied with ceramic junction (calomel)
Corning	476109	glass bodied with ceramic junction (calomel)
Orion (Ross)	800500	glass bodied reference half cell

Table 3. National Bureau of Standards (NBS) Salts for Reference Buffer Solutions.

NBS Standard Sample Designation	Buffer Salt	Drying Procedure
186-1-c	potassium dihydrogen phosphate	2 h in oven at 130°C
185-f	potassium hydrogen phthalate	2 h in oven at 110°C

The buffer salts listed above can be purchased from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

Table 4. Single-Operator Bias and Precision of pH Measurements Determined from Quality Control Check Samples.

Theoretical pH	Mean Measured pH	n[a]	Bias,[b] pH	Bias,[b] %	Precision,[b] s, pH	Precision,[b] RSD, %
3.61	3.63	15	0.02	0.6	0.01	0.3
4.30	4.32	72	0.02	0.5	0.01	0.2
5.60	5.42	80	-0.18	-3.2	0.04	0.7

The above data were obtained from records of pH measurements made under the direction of the NADP quality assurance program. The solutions used were a National Bureau of Standard (NBS) simulated rainwater sample (Research Material #8409-11, pH = 3.61), a 5.01 x 10^{-5} N nitric acid solution (pH = 4.30), and a 0.0005 M potassium chloride solution (pH = 5.60).

a. Number of replicates.

b. Calculations of bias and precision data were made using hydrogen ion concentrations.

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: pH

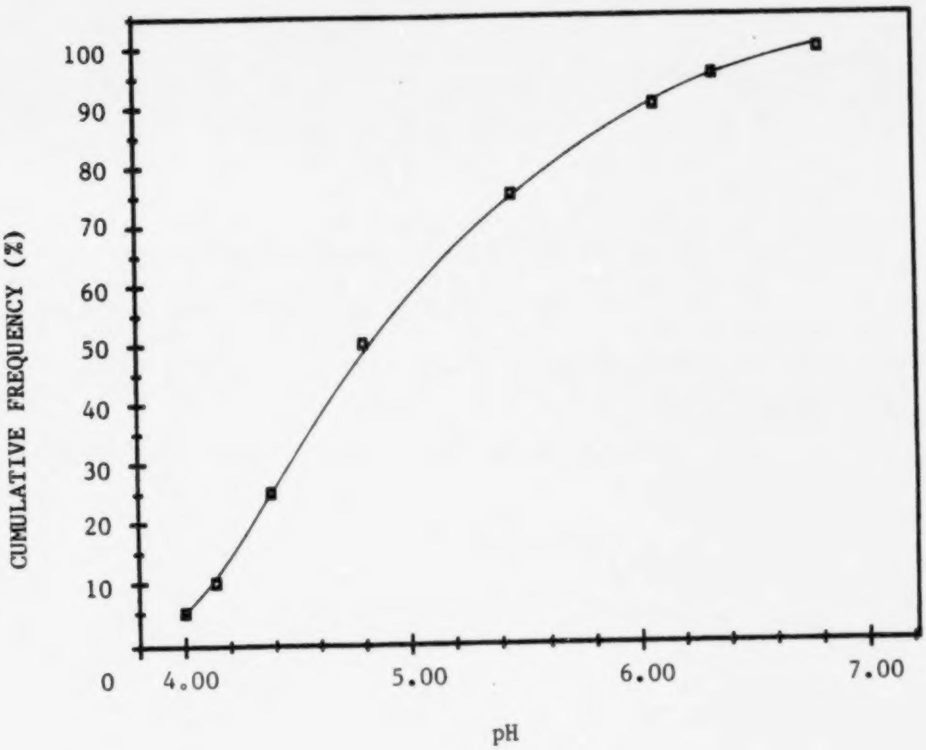
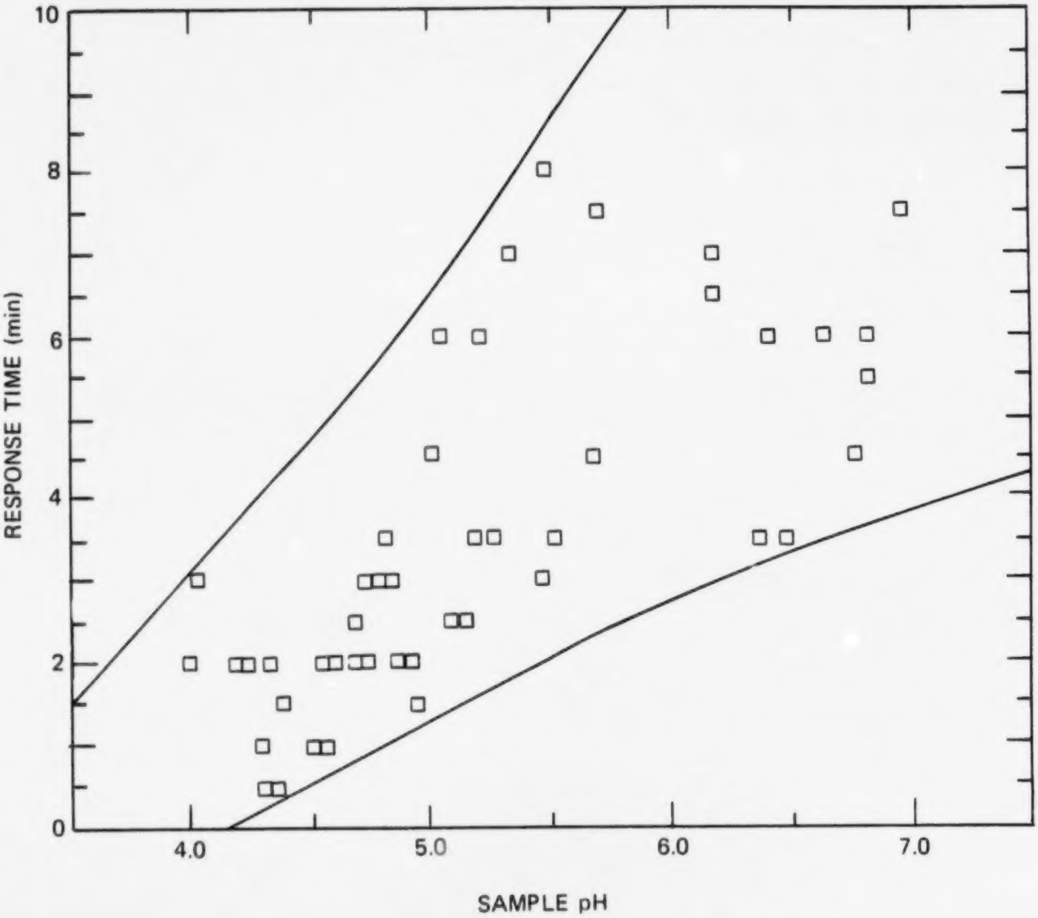


Figure 2. Time Required to Obtain Stable pH Response in Wet Deposition Samples.



Method 200.6 -- Dissolved Calcium, Magnesium, Potassium, and Sodium in Wet Deposition by Flame Atomic Absorption Spectrophotometry

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Performing Laboratory:

Loretta M. Skowron
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Method Detection Limits and Concentration Ranges for Flame Atomic Absorption Spectrophotometric Analysis of Wet Deposition.
2. Operating Conditions and Suggested Calibration Standard Concentrations for the Determination of Calcium, Magnesium, Potassium, and Sodium in Wet Deposition Samples.
3. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Analyte Spikes of Wet Deposition Samples.
4. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Quality Control Check Samples.

FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples: Calcium, Magnesium, Potassium, and Sodium.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of calcium, magnesium, potassium, and sodium in wet deposition by flame atomic absorption spectrophotometry (FAAS).

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limits (MDL) for the above analytes determined from replicate analyses of quality control check solutions containing 0.053 mg/L calcium, 0.018 mg/L magnesium, 0.012 mg/L sodium, and 0.013 mg/L potassium are 0.007, 0.002, 0.003, and 0.003 mg/L, respectively. The concentration range of this method is outlined in Table 1.

1.4 Figure 1 represents cumulative frequency percentile concentration plots of calcium, magnesium, potassium, and sodium obtained from the analysis of over five thousand wet deposition samples. These data should be considered during the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 A solution containing the element(s) of interest is aspirated as a fine mist into a flame where it is converted to an atomic vapor consisting of ground state atoms. These ground state atoms are capable of absorbing electromagnetic radiation over a series of very narrow, sharply defined wavelengths. A distinct line source of light, usually a hollow cathode lamp specific to the metal of interest, is used to pass a beam through the flame. Light from the source beam, less whatever intensity was absorbed by the atoms of the metal of interest, is isolated by the monochromator and measured by the photodetector. The amount of light absorbed by the analyte is quantified by comparing the light transmitted through the flame to light transmitted by a reference beam. The amount of light absorbed in the flame is proportional to the concentration of the metal in solution. The relationship between absorption and concentration is expressed by Beer's Law:

$$\log(I_o/I) = abc = A$$

where: I_o = incident radiant power
I = transmitted radiant power
a = absorptivity (constant for a given system)
b = sample path length
c = concentration of absorbing species (mg/L)
A = absorbance

The atomic absorption spectrophotometer is calibrated with standard solutions containing known concentrations of the element(s) of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

3. DEFINITIONS

3.1 **ABSORBANCE (A)** -- the logarithm to the base ten of the reciprocal of the transmittance, (T):

$$A = \log(1/T)$$

$$0.0044\ A = \text{the absorption of 1\% of the transmitted light.}$$

The absorbance is related to the analyte concentration by Beer's Law (Sect. 2.1) where $1/T = I_o/I$

3.2 **ATOMIC ABSORPTION** -- the absorption of electromagnetic radiation by an atom resulting in the elevation of electrons from their ground states to excited states. Atomic absorption spectrophotometry involves the measurement of light absorbed by atoms of interest as a function of the concentration of those atoms in a solution.

3.3 **SPECTRAL BANDWIDTH** -- the wavelength or frequency interval of radiation leaving the exit slit of a monochromator between limits set at a radiant power level half way between the continuous background and the peak of an emission line or an absorption band of negligible intrinsic width (14.1).

3.4 **SPECTROPHOTOMETER** -- an instrument that provides the ratio, or a function of the ratio, of the radiant power of two light beams as a function of spectral wavelength. These two beams may be separated in time and/or space.

3.5 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 Chemical interference is the most frequently encountered interference in atomic absorption spectrophotometry. A chemical interference may prevent, enhance, or suppress the formation of ground state atoms in the flame. For example, in the case of calcium determinations, the presence of phosphate or sulfate can result in the formation of a salt that hinders proper atomization of the solution when it is aspirated into the flame. This decreases the number of free, ground state atoms in the flame, resulting in lowered absorbance values. Aluminum can cause a similar interference when measuring magnesium. The addition of appropriate complexing agents to the sample solution reduces or eliminates chemical interferences and may increase the sensitivity of the method.

4.2 Alkali metals such as sodium and potassium may undergo ionization in an air-acetylene flame resulting in a decrease in ground state atoms available for measurement by atomic absorption. Addition of a large excess of an easily ionizable element such as cesium will eliminate this problem, since cesium will be preferentially ionized. The preferential ionization of the cesium [illegible] results in an enhanced atomic absorption signal for both potassium and sodium (14.3).

4.3 If a sample containing low concentrations of the metal being measured is analyzed immediately after a sample having a concentration exceeding the highest calibration standard, sample carry-over will result in elevated readings. To prevent this interference, routinely aspirate water (Sect. 7.2) for about 15 seconds after a high concentration sample. Depending on the concentration of metal in the last sample analyzed, it may be necessary to rinse for longer time periods. Complete purging of the system is ascertained by aspirating water until the absorbance readout returns to the baseline.

4.4 Wet deposition samples are characterized by low ionic strength and rarely contain enough salts to cause interferences due to nonspecific background absorbance. The use of background correction techniques is not necessary and will decrease the signal to noise ratio and lessen precision.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated hydrochloric acid (Sect. 7.5-6).

5.2 Use a fume hood, protective clothing, and safety glasses when preparing the lanthanum solution. The reaction between the lanthanum oxide and acid (Sect. 7.7) is extremely exothermic.

5.3 A permanent ventilation system is required to eliminate the large quantity of hot exhaust gases produced during instrument operation. Since acetylene is a flammable gas, take precautions when using it. To avoid explosions, never pass acetylene through copper or high-copper alloy (brass, bronze) fittings or piping.

5.4 The operator must wear safety glasses to avoid eye damage from the ultraviolet light emitted by the flame.

5.5 To avoid in-line explosions, do not allow the pressure of acetylene being delivered to the instrument to exceed 15 psig (10.6 g/m^2). In the event of a flashback, turn off the gas control switch, the instrument power, and the gas tanks.

5.6 Follow manufacturer's operating guidelines carefully when optimizing gas flow rates. Too low gas flow rates can result in a combustion within the gas mixing chamber and therefore a flashback.

5.7 Check that the drain tube from the gas mixing chamber, fitted with a safety trap, is filled with water before igniting the flame. Keep the drain tube filled to prevent explosion in the chamber. The safety trap may be either looped or valved.

5.8 Avoid any contact with a hot burner head. Serious tissue burns will result.

5.9 Follow American Chemical Society guidelines regarding safe handling of chemicals used in this method (14.4).

6. APPARATUS AND EQUIPMENT

6.1 ATOMIC ABSORPTION SPECTROPHOTOMETER -- Select a double-beam instrument having a dual grating monochromator, photodetector, pressure-reducing valves, adjustable spectral bandwith, wavelength range of 190-800 nm, and provisions for interfacing with a strip chart recorder or a suitable data system.

6.1.1 Burner -- Use a long path, single slot air-acetylene burner head supplied by the manufacturer of the spectrophotometer.

6.1.2 Hollow Cathode Lamps -- Single element lamps are recommended. Multi-element lamps are available but are not recommended. They generally have a shorter lifespan, are less sensitive, require a higher operating current, and increase the chances of spectral interferences. When available, electrodeless discharge lamps (EDL) may also be used.

6.1.3 Monochromator -- To increase sensitivity of calcium and potassium determinations, use a monochromator equipped with a blaze grating in the range of 500-600 nm (14.5). For the analysis of sodium and magnesium, a blaze grating in the range of 200-250 nm is adequate.

6.1.4 Photomultiplier Tube -- A wide spectral range (160-900 nm) phototube is recommended. Select a red-sensitive phototube to detect potassium at 766.5 nm and to increase sensitivity to calcium at 422.7 nm.

6.2 The first time any glassware is used for making stock solutions and standards, clean with 0.6 N HCl and rinse thoroughly with water (Sect. 7.2) before use. Maintain a set of Class A volumetric flasks to be used only when making dilute working standards for the analysis of wet deposition samples. Store filled with water (Sect. 7.2) and covered.

6.3 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. If a clean air bench is unavailable, samples must be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use chemicals of reagent grade or better for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.6). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 ACETYLENE (C_2H_2) -- Fuel -- Minimum acceptable acetylene purity is 99.5% (v/v). Change the cylinder when the pressure reaches 75 psig (53 g/m^2) if the acetylene is packed in acetone. Pre-purified grades that contain a proprietary solvent can be used to 30 psig (21 g/m^2) before replacement. Avoid introducing these solvents into the instrument. Damage to the instrument's plumbing system can result. Solvent in the system is indicated by abnormally high pulsating background noise. To prevent solvent carryover, allow acetylene cylinders to stand for at least 24 hours before use.

CAUTION: Acetylene is a highly flammable gas. Follow the precautions in Sect. 5.3-6 regarding safe operating pressures, suitable plumbing, and operator safety.

7.4 CESIUM SOLUTION (1.0 mL = 100.0 mg Cs) -- Ionization Suppressant -- Dissolve 126.7 g of cesium chloride (CsCl), dried at 105^{o}C for one hour, in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container. Add to samples and standards as directed in Sect. 9.4 and 11.4 for the determination of potassium and sodium.

7.5 HYDROCHLORIC ACID (6.0 N) -- Carefully add 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) to an equal volume of water (Sect. 7.2).

7.6 HYDROCHLORIC ACID (0.6 N) -- Add 50 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 900 mL of water (Sect. 7.2) and dilute to 1 L.

7.7 LANTHANUM SOLUTION (1.0 mL = 100.0 mg La) -- Releasing Agent -- In a glass 1 L volumetric flask, place 117.0 g of lanthanum oxide (La_2O_3), dried at 105°C for one hour. Add 6 N HCl very carefully to the solid in increments of about 0.5 mL. Cool the solution between additions. Continue adding the acid solution to the flask in increasing increments until a total of 500 mL of 6 N HCl has been added. Dilute to 1 L with water (Sect. 7.2). Store at room temperature in a high density polyethylene or polypropylene container. Add to samples and standards as directed in Sect. 9.4.3 and 11.4 for the determination of calcium and magnesium.

CAUTION: Dissolving lanthanum oxide in hydrochloric acid is a violently exothermic reaction; use extreme caution when dissolving the reagent. Refer to Sect. 5.2 for proper safety precautions when preparing this solution.

7.8 OXIDANT (air) -- The air may be provided by a compressor or commercially bottled gas supply. Remove oil, water, and other foreign matter from the air using a filter recommended by the manufacturer. Refer to the manufacturer's guidelines for recommended delivery pressure.

7.9 STOCK STANDARD SOLUTIONS -- Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as detailed below. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

7.9.1 Calcium Solution, Stock (1.0 mL = 1.0 mg Ca) -- Add 2.497 g of calcium carbonate ($CaCO_3$), dried at 180°C for one hour, to approximately 600 mL of water (Sect. 7.2). Add concentrated hydrochloric acid (HCl, sp gr 1.19) slowly until all the solid has dissolved. Dilute to 1 L with water (Sect. 7.2).

7.9.2 Magnesium Solution, Stock (1.0 mL = 1.0 mg Mg) -- Dissolve 1.000 g of magnesium ribbon in a minimal volume of 6 N HCl and dilute to 1 L with water (Sect. 7.2).

7.9.3 Potassium Solution, Stock (1.0 mL = 1.0 mg K) -- Dissolve 1.907 g of potassium chloride (KCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L.

7.9.4 Sodium Solution, Stock (1.0 mL = 1.0 mg Na) -- Dissolve 2.542 g of sodium chloride (NaCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L.

7.10 SAMPLE CONTAINERS -- Use polyolefin sample cups that have been thoroughly rinsed with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The dissolution of particulate materials can affect the stability of calcium, magnesium, sodium, and potassium in wet deposition samples (14.7). This instability generally results in a concentration increase for these constituents. Measurements should be made immediately after sample collection to obtain representative data. Refrigeration of samples at 4°C will minimize but not eliminate concentration changes.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is effective at stabilizing samples that are influenced by the dissolution of alkaline particulate matter (14.7). Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus. Filtered samples are stable for six weeks when stored at room temperature.

9. CALIBRATION AND STANDARDIZATION

9.1 SETTING INSTRUMENT PARAMETERS

9.1.1 Lamp Current -- Refer to manufacturer's guidelines for optimization of this parameter. The use of excessively high currents will shorten lamp life. High currents also cause line broadening, resulting in a reduction in sensitivity and calibration curve linearity, especially in the determination of magnesium. The use of currents that are too low will cause lamp instability and insufficient throughput of energy through the instrument's optical system. The result is increased signal noise due to excess electrical gain applied to the photodetector.

9.1.2 Light Beam -- Position a small card over the burner slot to intercept the light beam from the hollow cathode lamp. Check that the beam is focused midway along the slot and, if necessary, focus according to the manufacturer's guidelines. Rotate the lamp within its holder for maximum energy output readings.

9.1.3 Burner/Beam Alignment -- Position a small card over the burner slot to intercept the light beam from the hollow cathode lamp. For optimal sensitivity when analyzing calcium, magnesium, potassium, and sodium, adjust the burner height so that the center of the light beam is approximately 6 mm above the surface of the burner slot. By adjusting the burner alignment and rotation, set the light beam to coincide with the burner slot. While observing from above, move the card along the full length of the burner slot to ensure that the beam is centered over the slot for the entire length of the burner. Optimize this parameter for maximum instrumental sensitivity as directed in Sect. 9.2.

9.1.4 Wavelength -- Set the wavelength of the spectrophotometer for each analyte according to Table 2 by following the manufacturer's operating guidelines. After the instrument has warmed up with the flame burning (about 30 minutes), check the wavelength and readjust if necessary.

Note: The sodium spectrum is characterized by a doublet at 589.0 nm and 589.5 nm. The wavelength chosen for sodium determinations depends on the degree of analytical sensitivity desired by the operator. A setting of 589.0 nm will provide maximum sensitivity in the concentration range of most wet deposition samples. For those samples with higher sodium concentrations, a less sensitive setting of 589.5 nm is more appropriate. Refer to Tables 1 and 2 for information regarding working ranges, standards, and detection limits for sodium at each wavelength setting.

9.1.5 Spectral Bandwidth -- The selection of optimum bandwidth depends upon the spectrum of the particular element being analyzed. For the determination of calcium, magnesium, and potassium, a relatively wide (1.0 nm) bandwidth is appropriate. Because the sodium spectrum is characterized by a doublet, use a smaller bandwidth of 0.5 nm.

9.1.6 External Gas Settings -- Follow manufacturer's recommended delivery pressures for air and acetylene. Never allow acetylene pressure to exceed 15 psig (10.6 g/m^2).

9.1.7 Nebulization Rate -- Set the acetylene and air flow rates as recommended by the manufacturer. Adjust the nebulizer sample uptake rate to approximately 5 mL/min. If an adjustable glass bead nebulizer is used, adjust it according to manufacturer's guidelines. Exact placement of the glass bead is critical to ensure that a uniform vapor of the smallest size particles is introduced into the flame. Improper spacing of the bead from the nebulizer end will result in poor precision and sensitivity. Optimize the sample uptake rate for maximum sensitivity as directed in Sect. 9.2.

Note: The nebulizer can clog easily if particulates are present in the samples. Symptoms of this are decreased sensitivity and/or dramatically increased signal noise, especially noticeable at the higher concentration levels. A thorough cleaning with a small diameter wire is usually sufficient to unclog the nebulizer.

9.1.8 Flame Conditions -- If the flame temperature is too low, compounds containing the analyte will not be completely dissociated. Alternatively, too high a flame temperature may result in ionization. In both cases, a decrease in the apparent concentration of the analyte will result. In general, calcium exhibits maximum sensitivity at higher fuel and oxidant flow rates. Maximum sensitivity for potassium is obtained with minimal gas flow rates, resulting in lower flame temperature and allowing longer residence time of the atomic vapor in the flame. The MDLs stated in Sect. 1.3 for magnesium and sodium are obtained over a wide range of flame conditions. Optimize this parameter for maximum instrumental sensitivity as directed in Sect. 9.2.

CAUTION: Follow manufacturer's operating guidelines carefully when setting gas flow rates since combustion within the gas mixing chamber can occur if caution is not exercised.

9.2 Optimization -- Allow the instrument to warm up for 30 minutes before beginning the optimization. Set the instrument readout to absorbance units and set the integration time to <0.5 seconds. Use either a strip chart recorder or set the display in a continuous read mode to monitor absorbance readings. Aspirate a calibration standard at a concentration near the midpoint of the working range (Sect. 9.4). While watching the absorbance readings, adjust the instrument parameters with small, discrete changes until maximum values are obtained. Parameters such as flame conditions, nebulization rate, and the region of maximum atom concentration in the flame are interrelated. Adjustment of any of these three parameters usually requires adjustment of the other two.

9.3 Instrument Response Time -- Determine the minimum sample uptake time before taking a reading on a sample or standard solution. Use either a strip chart recorder or set the display in a continuous read mode to monitor absorbance readings. After purging the system with water (Sect. 7.2), aspirate the highest calibration standard (Sect. 9.4) and measure the length of time necessary to obtain a stable reading. Aspirate water (Sect. 7.2) and measure the time it takes for the baseline to return to zero.

Note: If the time necessary for the baseline to return to zero is longer than 15 seconds, a clogged nebulizer may be suspect. If purging time begins to increase during sample analysis, this may also be an indication of nebulizer clogging.

9.4 CALIBRATION SOLUTIONS

9.4.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte of interest at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of the analyte in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for each analyte are listed in Table 2.

9.4.2 Prepare all calibration standards by diluting the stock standards (Sect. 7.9) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The calibration standards are stable for three months if stored at room temperature in high density polyethylene or polypropylene containers.

9.4.3 After preparing the calibration standards to volume, add the lanthanum solution (Sect. 7.7) to the calcium and magnesium standards to yield 1000 mg/L La. Add the cesium solution (Sect. 7.4) to the potassium and sodium standards for 1000 mg/L Cs. Mix well. Use the same stock of ionization suppressant or releasing agent for the samples and the calibration standards.

Note: The final volume of each working standard solution exceeds the nominal volume by 1%. This adjustment is necessary to maintain consistency when the appropriate volume of suppressor solution is added to the wet deposition samples.

9.5 CALIBRATION

9.5.1 To establish a baseline, aspirate the zero standard and set the absorbance readout to 0.000. Aspirate the calibration standards, allowing time for each standard to equilibrate in the flame and gas mixing chamber before measuring the absorbance (Sect. 9.3). Construct calibration curves for each of the four analytes according to Sect. 12.

9.5.2 Analyze all the calibration standard solutions. The apparent concentration values must agree with the nominal concentrations within the predetermined control limits (Sect. 10.2.1) of three times the standard deviation (±3s). If results fall outside of these limits, recalibrate the instrument. If there is a consistent bias greater than $\bar{x} \pm 2s$ and less than $\bar{x} \pm 3s$, for all of the concentration values measured, reestablish the baseline with the zero standard and reanalyze the calibration standards.

9.5.3 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.7.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for precipitation measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.8). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of all the standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\overline{X}$) for determining the control limits. A warning limit of $\overline{X} \pm 2s$ and a control limit of $\overline{X} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.6 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 4. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.9), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentration of the analytes of interest. If any of the measured concentrations exceed the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Keep daily records of calibration data and the instrument operating parameters used at the time of data acquisition. Use these historical data as general performance indicators. Gross changes in sensitivity, curve linearity, or photomultiplier tube voltage are indicative of a problem. Possibilities include instrument malfunction, clogged nebulizer, incomplete optimization, bad hollow cathode lamp, contamination, and inaccurate standard solutions.

10.5 Precision will vary over the analyte concentration range. Standard deviation (s) increases as concentration increases while relative standard deviation (RSD) decreases. At approximately 100 times the MDL, the RSD should remain less than 1%.

10.6 Analyze a quality control check sample (QCS) after a calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). The check sample(s) selected must be within the range of the calibration standards. Prepare according to Sect. 11.4. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the spectrophotometer or calibration curve. Reestablish the baseline with the zero standard and/or recalibrate. If the QCS analysis is still beyond control limits, inaccurate working standards might be the problem. Prepare new standards. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.7 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze a zero standard and calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.6, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.6 and reanalyze all samples from the last time the measurement system was in control.

10.8 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.9 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.8). Compare the results obtained from the spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.10 Participation in performance evaluation studies is recommended for precipitation chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for precipitation chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

10.11 INSTRUMENT MAINTENANCE -- Strictly adhere to manufacturer's maintenance schedule.

10.11.1 Exposed optical mirrors should be replaced yearly to maintain optimal sensitivity and precision.

10.11.2 If the instrument is used for other sample types that have high analyte concentrations it may be necessary to disassemble the entire burner-nebulizer system for cleaning before analyzing wet deposition samples. This is best accomplished by placing the components in a water (Sect. 7.2) bath in an ultrasonic cleaner for a half hour. Rinse with water (Sect. 7.2) after cleaning and allow to air dry in a dust-free environment before reassembly. Check o-rings for wear and replace if necessary.

11. PROCEDURE

11.1 Set instrument parameters and optimize the instrument each day according to Sect. 9.1-2.

11.2 Prepare all standards and construct calibration curves according to Sect. 9.4-5.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.7.

11.4 Pipette the appropriate cesium or lanthanum solution into the empty sample cup (Cs or La:Sample = 1:100). For the determination of calcium and magnesium, use the lanthanum solution described in Sect. 7.7. For potassium and sodium determinations, add cesium solution (Sect. 7.4). Pour the sample into the sample cup containing Cs or La; 3 mL of sample for 30 uL of Cs or La is suggested. Mix well, aspirate, wait for equilibration in the flame (Sect. 9.3), and record the measured absorbance (or concentration).

11.5 If the absorbance (or concentration) for a given sample exceeds the working range of the system, dilute a separate sample with water (Sect. 7.2). Prepare and analyze according to Sect. 11.4.

11.6 When analysis is complete, rinse the system by aspirating water (Sect. 7.2) for ten minutes. Follow the manufacturer's guidelines for instrument shut-down.

12. CALCULATIONS

12.1 For each analyte of interest, calculate a linear least squares fit of the standard concentration as a function of the measured absorbance. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in mg/L
x = absorbance measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of absorbances measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9995 or greater. Determine the concentration of analyte of interest from the calibration curve.

12.2 If the relationship between concentration and absorbance is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9995. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of analyte of interest from the calibration curve.

12.3 An integration system or internal calibration software may also be used to provide a direct readout of the concentration of the analyte of interest.

12.4 Report concentrations in mg/L as Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+}. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.9). The results are summarized in Table 3. No statistically significant biases were found for any of the metal cations.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 4.

14. REFERENCES

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14.2 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1), "Excerpts from Standard for Metric Practice," Standard E 380-79, 1983, pp. 679-694.

14.3 Van Loon, J. C., Analytical Atomic Absorption Spectroscopy, Selected Methods Academic Press, Inc., New York, N. Y., 1980, p. 42.

14.4 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.5 Instrumentation Laboratory, Inc., *Operator's Manual Model IL951, AA/AE Spectrophotometer*, Instrumentation Laboratory, Inc., Wilmington, Massachusetts, 1982, pp. 3-4.

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14.7 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," *Atmos. Environ.* **12**, 1978, pp. 2343-2349.

14.8 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., *Quality Assurance Manual for Precipitation Measurement Systems*, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.9 *Annual Book of ASTM Standards*, Section 11, Vol. 11.01 (1), "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Method Detection Limits and Concentration Ranges for Flame Atomic Absorption Spectrophotometric Analysis of Wet Deposition.

Analyte	Method Detection Limit, mg/L	Concentration Range, mg/L
Calcium	0.007	0.030 - 3.00
Magnesium	0.002	0.010 - 1.00
Potassium	0.003	0.010 - 1.00
Sodium	0.003[a]	0.010 - 1.00[a]
	0.007[b]	0.020 - 2.00[b]

a. 589.0 nm wavelength setting
b. 589.5 nm wavelength setting

Table 2. Operating Conditions and Suggested Calibration Standard Concentrations for the Determination of Calcium, Magnesium, Potassium, and Sodium in Wet Deposition Samples.[a]

Analyte	Wavelength Setting, nm	Spectral Bandwidth, nm	Working Standards, mg/L
Calcium	422.7	1.0	zero 0.03 0.75 1.50 2.25 3.00
Magnesium	285.2	1.0	zero 0.01 0.25 0.50 0.75 1.00
Potassium	766.5	1.0	zero 0.01 0.25 0.50 0.75 1.00
Sodium[b]	589.0	0.5	zero 0.01 0.25 0.50 0.75 1.00
	589.5	0.5	zero 0.02 0.50 1.00 1.50 2.00

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a. Based on the MDL and 95th percentile concentration of each analyte obtained from analyses of over five thousand wet deposition samples from the NADP/NTN precipitation network.

b. Refer to Sect. 9.1.2 for details on wavelength selection

Table 3. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Calcium	0.087	20	101.5	0.001	0.010	No
	0.221	20	98.3	-0.003	0.011	No
Magnesium	0.018	20	97.2	-0.001	0.001	No
	0.045	20	96.6	-0.002	0.002	No
Potassium	0.021	18	145.2	0.010	0.006	No
	0.052	13	108.1	0.004	0.002	No
Sodium[c]	0.099	19	107.1	0.007	0.011	No
	0.249	20	100.2	0.000	0.008	No

a. Number of replicates
b. 95% Confidence Level
c. 589.0 nm wavelength

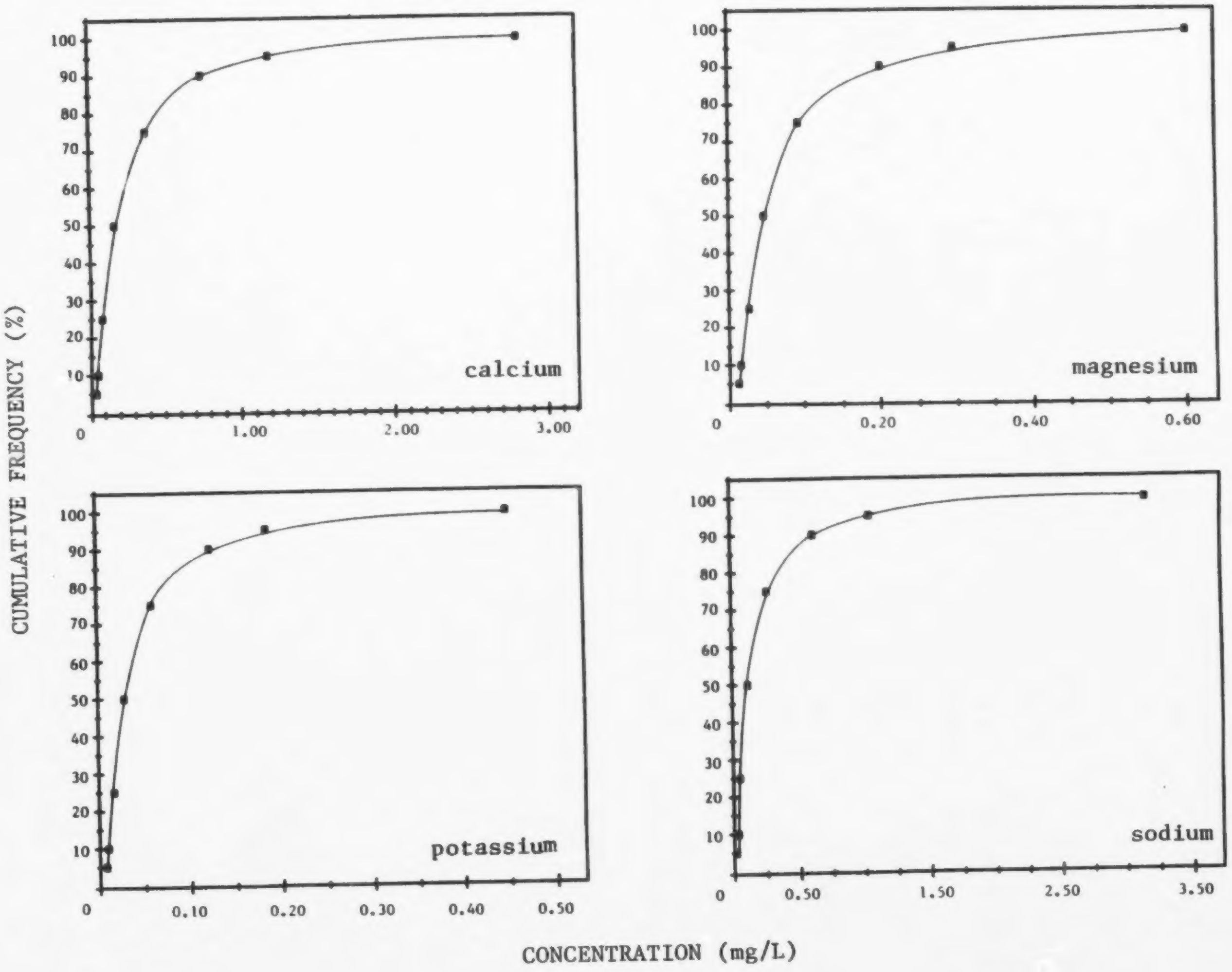
Table 4. Single-Operator Precision and Bias for Calcium, Magnesium, Potassium, and Sodium Determined from Quality Control Check Samples.

Analyte	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias,		Precision,	
				mg/L	%	s, mg/L	RSD, %
Calcium	0.053	0.051	145	-0.002	-3.8	0.002	3.9
	0.406	0.413	145	0.007	1.7	0.003	0.7
Magnesium	0.018	0.017	145	-0.001	-5.6	0.001	5.9
	0.084	0.083	145	-0.001	-1.2	0.001	1.2
Potassium	0.021	0.020	127	-0.001	-4.8	0.001	5.0
	0.098	0.095	122	-0.003	-3.1	0.001	1.0
Sodium[b]	0.082	0.084	123	0.002	2.4	0.001	1.2
	0.465	0.479	122	0.014	3.0	0.003	0.6

The above data were obtained from records of measurements made under the direction of the NADP quality assurance program.

a. Number of replicates
b. 589.0 nm wavelength

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Calcium, Magnesium, Potassium, and Sodium.



Method 300.6 -- Chloride, Orthophosphate, Nitrate and Sulfate in Wet Deposition by Chemically Suppressed Ion Chromatography

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Performing Laboratory:

Susan R. Bachman
Carla Jo Brennan
Jane E. Rothert
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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1. Method Detection Limits and Concentration Ranges for the Determination of Anions in Wet Deposition.
2. Compatibility of Separator and Suppressor Columns with Suggested Regeneration and Eluent Solutions for the Analysis of Wet Deposition.
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FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples.
2. Chromatogram of a Wet Deposition Sample Containing Chloride, Orthophosphate, Nitrate, and Sulfate, (a) Without and (b) With Eluent Matching.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of chloride, orthophosphate, nitrate, and sulfate in wet deposition by chemically suppressed ion chromatography.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limits (MDL) for the above analytes were determined from replicate analyses of calibration solutions containing 0.05 mg/L of each analyte. The measured MDL's for chloride, nitrate, and sulfate are 0.03 mg/L as Cl^-, NO_3^-, and SO_4^{-2}. The MDL for orthophosphate is 0.02 mg/L as PO_4^{-3}. The analyte concentration range of this method is outlined in Table 1.

1.4 Figure 1 represents cumulative frequency percentile concentration plots of chloride, nitrate, orthophosphate, and sulfate obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 Ion chromatography combines conductimetric detection with the separation capabilities of ion exchange resins. A filtered aliquot of sample, ranging in size from 100 to 250 uL, is pumped through an ion exchange column where the anions of interest are separated. Each ion's affinity for the exchange sites, known as its selectivity quotient, is largely determined by its radius and valence. Because different ions have different migration rates, the sample ions elute from the column as discrete bands. Each ion is identified by its retention time within the exchange column. The sample ions are selectively eluted off the separator column and onto a suppressor column. The eluent ions are neutralized and the sample ions are converted to their corresponding strong acids which are detected in a conductance cell. The chromatograms produced are displayed on a strip chart recorder or other data acquisition device for measurement of peak height or area. The ion chromatograph is calibrated with standard solutions containing known concentrations of the anion(s) of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

3. DEFINITIONS

3.1 ION EXCHANGE -- a reversible process by which ions are interchanged between an insoluble material and a liquid with no substantial structural changes of the material (14.1).

3.2 ELUENT -- the ionic liquid mobile phase used to transport the sample through the exchange columns.

3.3 REGENERANT -- a solution that converts and maintains an active form of the suppressor.

3.4 RESOLUTION -- the ability of a column to separate constituents under specified test conditions. Peak resolution is a function of column efficiency, selectivity, and capacity.

3.5 RETENTION TIME -- the interval measured from the point of sample injection to the point of maximum peak height or area.

3.6 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 Unresolved peaks will result when the concentration of one of the sample components is 10 to 20 times higher than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or the flow rate may correct this problem.

4.2 Interferences can be caused by ions with retention times that are similar to and thus overlap those of the anion of interest. This type of positive interference is rare in wet deposition samples. If this interference occurs, decreasing the eluent concentration or the flow rate may result in improved peak resolution.

4.3 Water from the sample injection will cause a negative peak or dip in the chromatogram when it elutes because its conductance is less than that of the suppressed eluent. Any ion of interest eluting near the water dip must be sufficiently resolved from the dip to be accurately quantified. This can be achieved by changing the eluent concentration or decreasing the flow rate. Alternatively, the negative peak can be reduced by adding an equivalent of 100 uL of a prepared eluent concentrate (solution that is 100 times more concentrated than the eluent used for analysis) per 10.0 mL of sample. Proportionate eluent additions must also be included in calibration and quality control solutions.

4.4 Deterioration in column performance can result from the buildup of contaminants on the exchange resin. Losses in retention and resolution are symptoms of column deterioration. Refer to the manufacturer's guidelines for instructions on cleaning the column resin.

4.5 The presence of air bubbles in the columns, tubing, or conductivity detector cell will cause baseline and peak variability. Avoid introducing air into the system when injecting samples and standards. Using degassed eluents and regenerants will help to minimize the introduction of air.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated sulfuric acid (Sect. 7.4).

5.2 Keep the doors of the instrument column compartment closed at all times when pumps and columns are in use to prevent injury to the operator from column explosion if the pump pressure or column backpressure increases.

5.3 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.3).

6. APPARATUS AND EQUIPMENT

6.1 ION CHROMATOGRAPH -- Select an instrument equipped with an injection valve, sample loop, a sampling system, analytical columns, compressed gas, pumps, detector, and strip chart recorder or other data acquisition device. All tubing that comes in contact with samples and standards must be manufactured from inert material such as polyethylene or tetrafluoroethylene (TFE). Refer to Table 2 for details on column compatibility.

6.1.1 Anion Guard Column -- Place before the separator column. This contains the same resin as the separator column and is used to protect the ion exchange column from being fouled by particulates or organic constituents. Using an anion guard column will prolong the life of the separator column (4 x 50 mm, Dionex P/N 030986, AG3, or equivalent).

6.1.2 Anion Separator Column -- This is a column packed with a pellicular low-capacity anion exchange resin constructed of polystyrene-divinylbenzene beads coated with ammonium active sites (4 x 250 mm, Dionex P/N 030985, AS3, or equivalent).

6.1.3 Anion Suppressor Column -- Place after the separator column. This may be in the form of a packed bed, fiber or micro-membrane suppressor. The first type of suppressor is packed with a high-capacity anion exchange resin in the protonated form capable of converting the eluent to a low or negligible background conductance and converting the sample anions to their corresponding strong acids (Dionex P/N 030828, ASC2, or equivalent). The second two types of suppressors utilize a semipermeable membrane containing anion exchange sites to suppress eluent conductance. Both the fiber and micro-membrane suppressors are under continuous regeneration. (Dionex P/N 35350, AFS, fiber; Dionex P/N 38019, AMMS, micro-membrane, or equivalent).

6.1.4 Compressed Gas (Nitrogen or Air) -- Use ultra-high purity, 99.999% (v/v) compressed gas conforming to the recommendations of the manufacturer of the ion chromatograph.

6.1.5 Detector -- Select a flow-through, temperature-compensated, electrical conductance cell with a volume of approximately 6 uL coupled with a meter capable of reading from 0 to 1000 uS/cm on an analog or digital scale.

6.1.6 Pump -- Use a pump capable both of delivering an accurate flow rate and of tolerating the optimal pressure as suggested by the instruction manual accompanying the ion chromatograph and columns selected. A constant pressure, constant flow pump is recommended for enhanced baseline stability. All interior pump surfaces that will be in contact with samples and standards should be manufactured from inert materials.

6.1.7 Recorder -- This should be compatible with the maximum conductance detector output with a full-scale response time of 0.5 sec or less.

6.1.8 Sample Loop -- Select a sample loop compatible with the column system having a capacity of 100-250 uL.

6.1.9 Sampling System -- Select one of the following for sampling.

6.1.9.1 Syringe -- Use a syringe equipped with a male fitting with a minimum capacity of 2 mL.

6.1.9.2 Autosampler -- Use an autosampling system capable of precise delivery, equipped with a dust cover to prevent airborne contamination.

6.2 ELUENT AND REGENERANT RESERVOIRS -- Select containers with a 4-20 L capacity that are designed to minimize introduction of air into the flow system. The regenerant reservoirs may be pressurized with nitrogen or air (5-10 psi) to ensure constant delivery to the suppressor column.

6.3 INTEGRATOR (optional) -- Select an instrument compatible with the detector output to quantitate the peak height or area. A system such as the Spectra Physics 4270 Integrator or a personal computer with a chromatographic software package such as furnished by Nelson Analytical, may be used to provide a direct readout of the concentration of the analyte of interest. If an integrator is used, the maximum peak height or area measurement must be within the linear range of the integrator.

6.4 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Room temperature fluctuations should be controlled to within ±3°C to prevent baseline drift and changes in detector response. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.4). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions. Degas the water prior to use by placing in a glass container, agitating vigorously, and aspirating off the liberated gases.

7.3 ELUENT SOLUTION -- Sodium bicarbonate 0.0056 N, sodium carbonate 0.0044 N (eluent strength recommended for wet deposition analysis using an AS3 or AS4 separator column). Dissolve 0.941 g sodium bicarbonate ($NaHCO_3$) and 0.933 g of sodium carbonate (Na_2CO_3) in water (Sect. 7.2) and dilute to 4 L. Mix the solution well and degas before use. Refer to Table 2 for a list of suitable eluent solutions for other separator columns.

7.4 REGENERATION SOLUTION -- Dilute concentrated sulfuric acid (H_2SO_4, sp gr 1.84) to one of the following concentrations for use with packed bed, fiber, or micro-membrane suppressors.

7.4.1 Sulfuric Acid (1.0 N) -- (regenerant for a packed bed column) Add 111 mL of concentrated H_2SO_4 to 2 L of water (Sect. 7.2) and dilute to 4 L.

7.4.2 Sulfuric Acid (0.025 N) -- (regenerant for a fiber suppressor) Add 2.8 mL of concentrated H_2SO_4 to 2 L of water (Sect. 7.2) and dilute to 4 L.

7.4.3 Sulfuric Acid (0.018 N) -- (regenerant for a micro-membrane suppressor) Add 2.0 mL of concentrated H_2SO_4 to 2 L of water (Sect. 7.2) and dilute to 4 L.

7.5 STOCK STANDARD SOLUTIONS -- Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as listed below. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

7.5.1 Chloride Solution, Stock (1.0 mL = 1.0 mg Cl) -- Dissolve 1.6484 g of sodium chloride (NaCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L.

7.5.2 Nitrate Solution, Stock (1.0 mL = 1.0 mg NO_3)-- Dissolve 1.3707 g sodium nitrate ($NaNO_3$) in water (Sect. 7.2) and dilute to 1 L.

7.5.3 Orthophosphate Solution, Stock (1.0 mL = 1.0 mg PO_4) -- Dissolve 1.4328 g anhydrous potassium phosphate (KH_2PO_4) in water (Sect. 7.2) and dilute to 1 L.

7.5.4 Sulfate Solution, Stock (1.0 mL = 1.0 mg SO_4) -- Dissolve 1.8142 g anhydrous potassium sulfate (K_2SO_4) in water (Sect. 7.2) and dilute to 1 L.

7.6 SAMPLE CONTAINERS -- Use polyolefin or glass sample cups that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 Chloride is the only anion in this method that is stable in solution (14.5). Nitrate and orthophosphate concentrations are affected by biological activity within wet deposition samples. The oxidation of nitrite and sulfite after sample collection will result in increased concentrations of nitrate and sulfate, respectively. Sample measurements for sulfate, nitrate, and orthophosphate ions should be made immediately after collection if possible. Refrigeration of samples at 4°C will minimize, but not eliminate, concentration changes prior to chemical analysis (14.5).

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is partially effective at stabilizing nitrate and orthophosphate by removal of biologically active species. Refrigeration after immediate filtration is the most reliable method to ensure sample integrity for these two parameters. Sample storage time should not exceed one week. Chloride and sulfate determinations should be made within two weeks of sample collection.

9. CALIBRATION AND STANDARDIZATION

9.1 Assemble the ion chromatograph according to the manufacturer's instructions. Recommended operating conditions for the apparatus are listed in Table 1. Included in Table 3 are retention times characteristic of this method. Other columns, chromatographic conditions, or detectors may be used provided the requirements detailed in Sect. 6 are met.

9.2 Bring all standards, samples, eluents, and regenerants to ambient temperature before beginning any analyses. Maintain laboratory temperature conditions within ±3°C while conducting analyses.

9.3 Use the eluent strength in Sect. 7.3 for wet deposition analyses. If peak resolution is not adequate, it may be necessary to decrease the eluent strength. Refer to the manufacturer's recommendations for guidelines on optimizing eluent strength.

9.4 Adjust the instrument flow rate for optimal peak resolution. Decreasing the flow rate may provide improved peak resolution but will lengthen retention times. Increasing the flow rate decreases peak resolution and shortens retention times. Refer to the manufacturer's recommendations for guidelines on optimizing flow rate.

9.5 Equilibrate the system by pumping eluent through all the columns and the detector until a stable baseline is obtained.

9.6 CALIBRATION SOLUTIONS

9.6.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte(s) of interest at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of the analyte in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. If a second detector sensitivity scale setting is used to increase the instrument's concentration range, calibrate at the two sensitivity levels. Suggested calibration standards for each analyte are listed in Table 3.

9.6.2 Prepare all calibration standards by diluting the stock standards (Sect. 7.5). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. Standards with a concentration greater than 0.10 mg/L of each anion are stable for one week when stored at room temperature in high density polyethylene or polypropylene containers. Prepare standards with 0.10 mg/L or less of each anion fresh every day and store at room temperature in high density polyethylene or polypropylene containers.

9.6.3 Chloride, orthophosphate, nitrate, and sulfate can be combined into a single solution at each of the five standard concentration levels.

9.7 CALIBRATION CURVE

9.7.1 Flush the sampling system with the calibration standard using at least ten times the injection loop volume. Inject the standard and record the peak height or area response. Repeat this step for each calibration standard. Construct calibration curves for each of the four analytes according to Sect. 12.

9.7.2 Record the retention times for each analyte. Measure retention time from an initial starting point on the chromatogram.

9.7.3 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.5.

9.7.4 Whenever a new eluent or regenerant solution is made, reestablish the calibration curve.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.6). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\overline{x}$) for determining the control limits. A warning limit of $\overline{x} \pm 2s$ and a control limit of $\overline{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of 10 analyses performed on 10 days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.4 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 5. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of 10 analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using ±2s and ±3s, respectively. If the data indicate that no significant method bias exists (14.7), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentrations of the anions that will be measured in wet deposition. If any of the analyte concentrations exceed the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample (QCS) after the ion chromatograph has been calibrated. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive

QCS checks are outside of the ±2s limits, a problem is indicated with the ion chromatograph or calibration curve. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.6). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Check the instrumental operating parameters each day according to Sect. 9 and Table 1.

11.2 Prepare all standards and construct calibration curves according to Sect. 9.6 and 9.7.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.4 SAMPLE INJECTION

11.4.1 Use the same size injection loop for both standards and samples. Samples may be injected manually with a syringe or with an autosampler.

11.4.2 Flush the sampling system thoroughly with each new sample using a rinse volume of at least ten times the loop size. Inject the sample, avoiding the introduction of air bubbles into the system.

11.4.3 Record the resulting peak heights or areas.

11.5 If the peak height or area response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.6 A sample chromatogram is provided in Figure 2.

12. CALCULATIONS

12.1 For each analyte of interest, calculate a linear least squares fit of the standard concentrations as a function of the measured peak height or area. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in mg/L
x = peak height or area measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of peak heights or areas measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of the analyte of interest from the calibration curve.

12.2 If the relationship between standard concentration and measured peak height or area is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2 x^2 + B_1 x + B_0$$

A computer program is necessary for the derivation of this function. Determine the concentration of the analyte of interest from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of the analyte of interest.

12.4 Report data in mg/L as Cl^-, NO_3^-, PO_4^{-3}, or SO_4^{-2}. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.7). The results are summarized in Table 4. No statistically significant biases were found for any of the four inorganic anions.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 5.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1), "Definitions of Terms Related to Water," Standard D 1129-82b, 1983, p. 4.

14.2 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.3 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.4 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.5 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. 12, 1978, pp. 2343-2349.

14.6 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.7 Annual Book of ASTM Standards, Section 11, Vol. 11.01 (1), "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Method Detection Limits and Concentration Ranges for the Determination of Anions in Wet Deposition.

Analyte	Method Detection Limit,[a] mg/L	Concentration Range, mg/L
Chloride	0.03	0.03 - 2.00
Orthophosphate	0.02	0.02 - 0.25
Nitrate	0.03	0.03 - 5.00
Sulfate	0.03	0.03 - 8.00

a. Chromatographic Conditions:
Guard Column -- Dionex AG3
Separator Column -- Dionex AS3
Fiber Suppressor -- Dionex AFS
Detector -- As specified in 6.1.5
Eluent -- As specified in 7.3
Sample Loop -- 250 uL
Flow Rate -- 3 mL/min
Detector Sensitivity -- 10 uS/cm

Table 2. Compatibility of Separator and Suppressor Columns with Suggested Regeneration and Eluent Solutions for the Analysis of Wet Deposition.

Anion Separator Column	Eluent Solution	Anion Suppressors Packed Bed	 Fiber	 Micro-membrane
Dionex AS1	0.003 M $NaHCO_3$ 0.0024 M Na_2CO_3	compatible	compatible	not recommended[a]
Dionex AS3	0.0028 M $NaHCO_3$ 0.0022 M Na_2CO_3	compatible	compatible	not recommended[a]
Dionex AS4	0.0028 M $NaHCO_3$ 0.0022 M Na_2CO_3	compatible	compatible	compatible
Dionex AS4A	0.00075 M $NaHCO_3$ 0.0022 M Na_2CO_3	compatible	compatible	compatible

a. The increased back-pressure created by the micro-membrane suppressor may reduce column efficiency when this type of separator column is used. Refer to the manufacturer's guidelines for recommendations of minor adjustments necessary to make this system work properly.

Regeneration Solutions:

Packed Bed -- 0.1 N HCl or 1.0 N H_2SO_4
Fiber -- 0.025 N H_2SO_4
Micro-membrane -- 0.018 N H_2SO_4

Table 3. Retention Times and Suggested Calibration Standard Concentrations for the Determination of Anions in Wet Deposition Samples.[a]

Analyte	Approximate Retention Time Range,[b] sec	Calibration Standards, mg/L
Chloride	84 - 120	zero
		0.03
		0.40
		0.75
		1.10
		1.50
Orthophosphate	144 - 180	zero
		0.02
		0.10
		0.15
		0.20
		0.25
Nitrate	240 - 300	zero
		0.03
		1.00
		2.00
		3.00
		4.00
Sulfate	336 - 396	zero
		0.03
		1.25
		2.50
		3.75
		5.00

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a. Based on the MDL and 95th percentile concentrations of each analyte obtained from analyses of over five thousand wet deposition samples from the NADP/NTN precipitation network.

b. The retention time was measured from the time of injection. For chromatographic conditions, refer to Table 1.

Table 4. Single-Operator Precision and Bias for Chloride, Orthophosphate, Nitrate, and Sulfate Determined from Analyte Spikes of Wet Deposition Samples.[a]

Analyte	Amount Added, mg/L	n[b]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[c]
Chloride	0.10	10	102.0	0.00	0.01	No
	0.32	9	101.8	0.01	0.02	No
Ortho-phosphate	0.11	10	98.3	0.00	0.01	No
Nitrate	0.44	10	99.8	0.00	0.03	No
	1.10	10	96.0	-0.04	0.07	No
Sulfate	0.46	10	101.3	0.01	0.04	No
	1.10	10	98.7	-0.01	0.05	No

---

a. Chromatographic Conditions:
    Guard Column -- Dionex AG3
    Separator Column -- Dionex AS3
    Packed Bed Suppressor Column -- Dionex ASC2
    Detector -- As specified in 6.1.5
    Eluent -- As specified in 7.3
    Sample Loop -- 250 uL
    Flow Rate -- 3 mL/min
    Detector Sensitivity -- 10 uS/cm

b. Number of replicates

c. 95% Confidence Level

Table 5. Single-Operator Precision and Bias for Chloride, Orthophosphate, Nitrate, and Sulfate Determined from Quality Control Check Samples.[a]

				Bias,		Precision,	
Analyte	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[b]	mg/L	%	s, mg/L	RSD, %
Chloride	0.18	0.19	132	0.01	5.6	0.02	10.5
	0.85	0.87	479	0.02	2.4	0.03	3.4
	1.78	1.88	255	0.10	5.6	0.05	2.7
Orthophosphate	0.05	0.05	10	0.00	0.0	0.00	0.0
	0.15	0.15	10	0.00	0.0	0.01	6.7
Nitrate	0.80	0.81	485	0.01	1.2	0.02	2.5
	3.54	3.64	415	0.10	2.8	0.12	3.3
Sulfate	0.72	0.72	340	0.00	0.0	0.03	4.2
	0.94	0.92	482	-0.02	-2.1	0.03	3.3
	3.60	3.69	122	0.09	2.5	0.11	3.0

The above data were obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

a. For chromatographic conditions, refer to Table 1.
b. Number of replicates

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Chloride, Orthophosphate, Nitrate, and Sulfate.

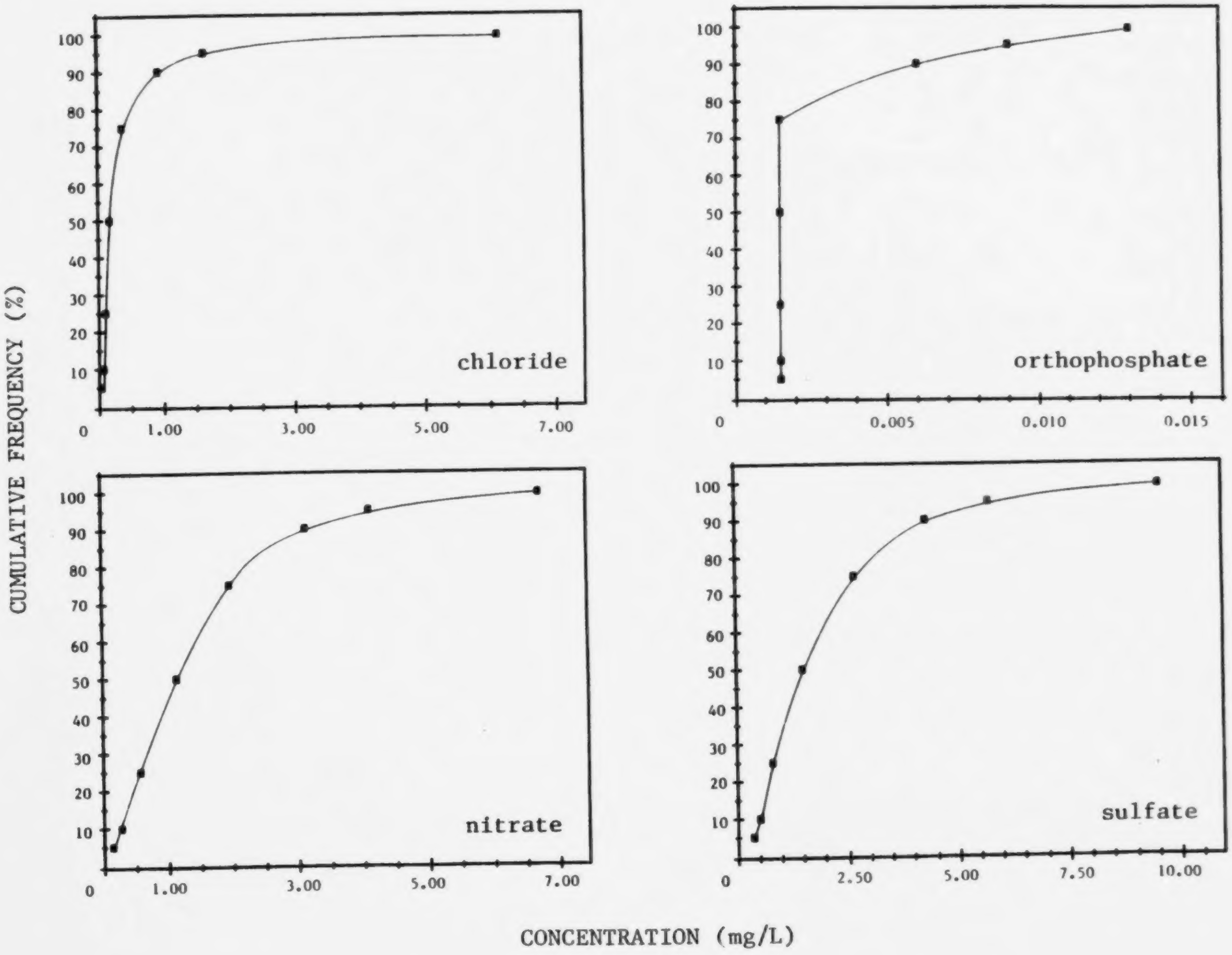
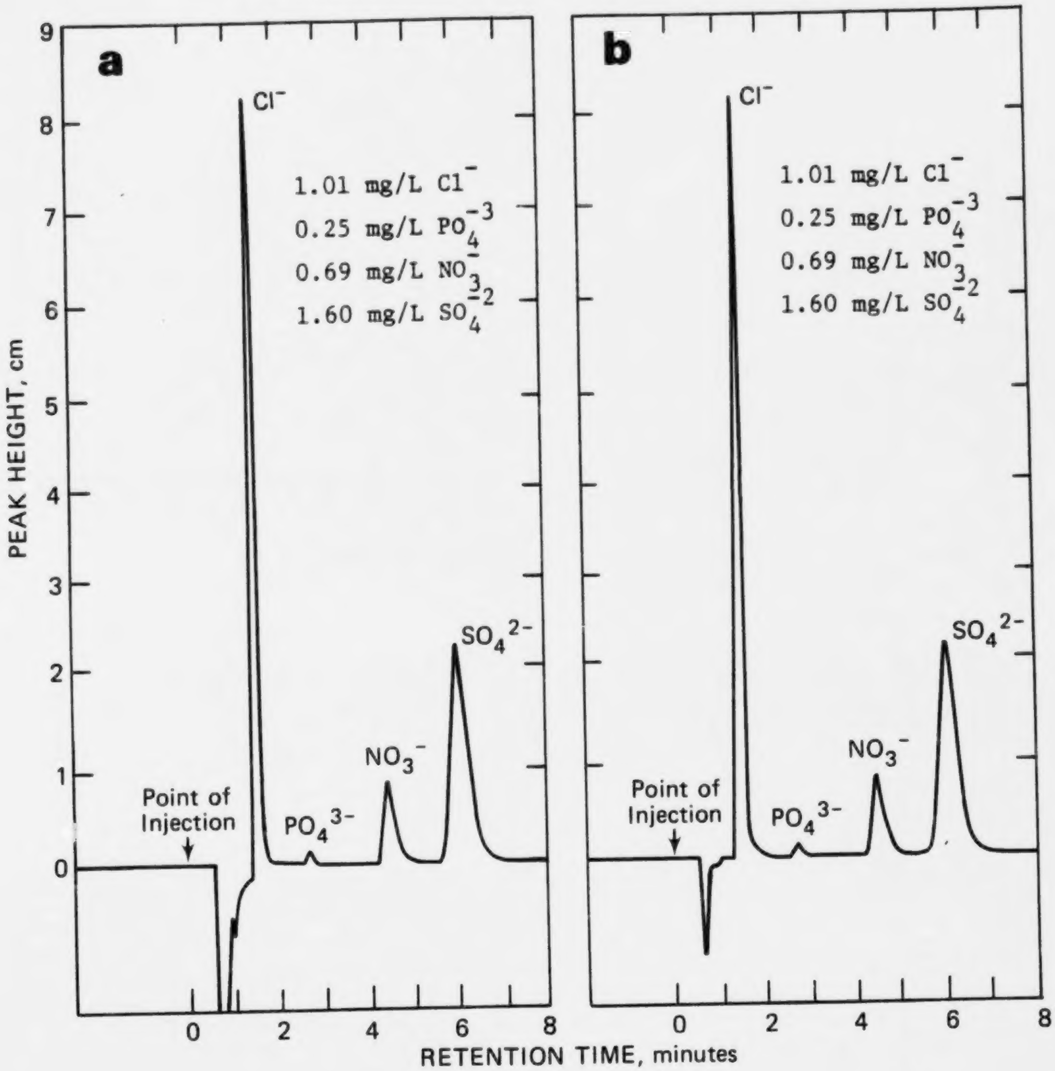


Figure 2. Chromatogram of a Wet Deposition Sample Containing Chloride, Orthophosphate, Nitrate, and Sulfate, (a) Without and (b) With Eluent Matching.



Chromatographic Conditions:
- Guard Column -- Dionex AG3
- Separator Column -- Dionex AS3
- Fiber Suppressor -- Dionex AFS
- Detector -- As specified in 6.1.5
- Eluent -- As specified in 7.3
- Sample Loop -- 250 μL
- Flow Rate -- 3 mL/min
- Detector Sensitivity -- 10 μS/cm

Method 300.7 -- Dissolved Sodium, Ammonium, Potassium, Magnesium, and Calcium in Wet Deposition by Chemically Suppressed Ion Chromatography

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Performing Laboratory:

Susan R. Bachman
Jane E. Rothert
Brian Kaiser
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples.
2. Chromatogram of a Calibration Standard Containing Sodium, Ammonium, and Potassium.
3. Chromatogram of a Calibration Standard Containing Magnesium and Calcium.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the determination of sodium, ammonium, potassium, magnesium, and calcium in wet deposition by chemically suppressed ion chromatography.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limits (MDL) for the above analytes determined from replicate analyses of quality control check solutions are 0.02 mg/L for magnesium and calcium, 0.03 mg/L for sodium and ammonium, and 0.01 mg/L for potassium. The concentration of analyte in each check sample is detailed in Table 4. The applicable analyte concentration range of this method is outlined in Table 1.

1.4 Figure 1 represents cumulative frequency percentile concentration plots of sodium, ammonium, potassium, magnesium, and calcium obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 Ion chromatography combines conductimetric detection with the separation capabilities of ion exchange resins. A filtered 100 uL aliquot of sample is pumped through an ion exchange column where the cations of interest are separated. Each ion's affinity for the exchange sites, known as its selectivity quotient, is largely determined by its radius and valence. Because different ions have different migration rates, the sample ions elute from the column as discrete bands. Each ion is identified by its retention time within the exchange column. The sample ions are selectively eluted off the separator column and onto a suppressor column. The eluent ions are neutralized and the sample ions are converted to their corresponding strong bases which are detected in a conductance cell. The chromatograms produced are displayed on a strip chart recorder or other data acquisition device for measurement of peak height or area. The ion chromatograph is calibrated with standard solutions containing known concentrations of the cation(s) of interest. Calibration curves are constructed from which the concentration of each analyte in the unknown sample is determined.

3. DEFINITIONS

3.1 ION EXCHANGE -- a reversible process by which ions are interchanged between an insoluble material and a liquid with no substantial structural changes of the material (14.1).

3.2 ELUENT -- the ionic liquid mobile phase used to transport the sample through the exchange columns.

3.3 REGENERANT -- a solution that converts and maintains an active form of the suppressor.

3.4 RESOLUTION -- the ability of a column to separate constituents under specified test conditions. Peak resolution is a function of column efficiency, selectivity, and capacity.

3.5 RETENTION TIME -- the interval measured from the point of sample injection to the point of maximum peak height or area.

3.6 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 Unresolved peaks will result when the concentration of one of the sample components is 10 to 20 times higher than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or the flow rate may correct this problem.

4.2 Interferences may be caused by ions with retention times that are similar to and thus overlap those of the cation of interest. This type of positive interference is rare in wet deposition samples. If this type of interference occurs, decreasing the eluent concentration or the flow rate may improve peak resolution.

4.3 The divalent cations, present in solution, which are not eluted with the monovalent cation eluent, will cause a loss of retention and resolution of the monovalent species, as they accumulate on the separator column. When this occurs, clean the monovalent column with 20 mL of 1.0 N HCl for 15 minutes and then equilibrate by rinsing the column with eluent until a stable baseline is obtained.

4.4 Deterioration in column performance may result from the buildup of contaminants on the exchange resin. Losses in retention and resolution are symptoms of column deterioration. Refer to the manufacturer's guidelines for instructions on cleaning the column resin.

4.5 The presence of air bubbles in the columns, tubing, or conductivity detector cell will cause baseline and peak variability. Avoid introducing air into the system when injecting samples and standards. Using degassed eluents and regenerants will help to minimize the introduction of air.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated hydrochloric acid (Sect. 7.3-7.4).

5.2 Keep the doors of the instrument column compartment closed at all times when pumps and columns are in use to prevent injury to the operator from column explosion if the pump pressure or column backpressure increases.

5.3 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.3).

6. APPARATUS AND EQUIPMENT

6.1 ION CHROMATOGRAPH -- Select a chromatograph equipped as detailed in Sects. 6.1.1-6.1.9. To determine monovalent and divalent cations simultaneously, select a dual channel chromatograph equipped with two separator and two suppressor columns. If the sample ions are to be determined sequentially by analyzing the sample twice, the same suppressor column may be used for both determinations. The divalent eluent solution is strongly retained on the guard and separator columns, making the determination of monovalent ions after divalent ions with the same guard and separator columns impractical. Therefore, use two different sets of cation guard and separator columns; one set should be dedicated to the determination of monovalent and the other to divalent cations.

6.1.1 Cation Guard Column -- Place before the separator column. This contains the same resin as the separator column and is used to protect the ion exchange column from being fouled by particulates or organic constituents (4 x 50 mm, Dionex P/N 30830, CG1, or equivalent). Using a cation guard column will prolong the life of the separator column.

6.1.2 Cation Separator Column -- This is a column packed with a pellicular low-capacity cation exchange resin containing polystyrene-divinylbenzene beads coated with sulfate active sites (4 x 250 mm, Dionex P/N 30831, CS1, or equivalent).

6.1.3 Cation Suppressor Column -- Place after the separator column. This may be in the form of a packed bed, a fiber, or a micro-membrane suppressor. The first type of suppressor is packed with a high-capacity cation exchange resin in the unprotonated form capable of converting the eluent to a low or negligible background conductance and converting the sample cations to their corresponding strong bases (Dionex P/N 30834, CSC2, or equivalent). The second two types of suppressors utilize a semipermeable membrane containing cation exchange sites to suppress eluent conductance (Dionex P/N 35352, CFS, fiber; Dionex P/N 37076, CMMS, micro-membrane; or equivalent). Both the fiber and micro-membrane suppressors are under continuous regeneration.

6.1.4 Compressed Gas (Nitrogen or Air) -- Use ultra-high purity 99.999% (v/v) compressed gas conforming to the recommendations of the manufacturer of the ion chromatograph.

6.1.5 Detector -- Select a flow-through, temperature-compensated, electrical conductance cell with a volume of approximately 6 uL coupled with a meter capable of reading from 0 to 1000 uS/cm on an analog or digital scale.

6.1.6 Pump -- Use a pump capable both of delivering an accurate flow rate and of tolerating the optimal pressure suggested by the instruction manual accompanying the ion chromatograph and columns selected. A constant pressure, constant flow pump is recommended for enhanced baseline stability.

6.1.7 Recorder -- This should be compatible with the maximum detector output with a full-scale response time in 0.5 sec or less.

6.1.8 Sample Loop -- Select a sample loop compatible with the column system having a capacity of 100 uL for optimal sensitivity in wet deposition analyses.

6.1.9 Sampling System -- Select one of the following for sampling.

6.1.9.1 Syringe -- Use a syringe equipped with a male fitting having a minimum capacity of 2 mL.

6.1.9.2 Autosampler -- Use an autosampling system capable of precise delivery, equipped with a dust cover to prevent airborne contamination.

6.2 ELUENT AND REGENERANT RESERVOIRS -- Select containers with a 4-20 L capacity that are designed to minimize introduction of air into the flow system. The regenerant reservoirs may be pressurized with nitrogen or air (5-10 psi) to ensure constant delivery to the suppressor column.

6.3 INTEGRATOR (optional) -- Select an instrument compatible with the detector output to quantitate the peak height or area. A system such as the Spectra Physics 4270 Integrator or a personal computer with a chromatographic software package such as furnished by Nelson Analytical, may be used to provide a direct readout of the concentration of the analyte of interest. If an integrator is used, the maximum height or area measurement must be within the linear range of the integrator.

6.4 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room. Maintain laboratory temperature within ±3 °C to minimize baseline drift and changes in detector response.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.4). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions. Degas the water prior to use by placing in a glass container, agitating vigorously, and aspirating off the liberated gases.

7.3 ELUENT SOLUTION -- For the determination of monovalent cations (sodium, ammonium, and potassium), use a dilute (0.005 N) hydrochloric acid (HCl) eluent. For the determination of divalent cations (magnesium and calcium), use a solution of 0.002 N HCl and 0.004 N meta phenylenediamine Dihydrochloride (mPDA 2HCl).

7.3.1 Hydrochloric Acid (0.005 N) -- (eluent solution for monovalent cations) Add 1.65 mL of concentrated HCl (sp gr 1.19) to 500 mL of water (Sect. 7.2) and dilute to 4 L.

7.3.2 Hydrochloric Acid : meta Phenylenediamine Dihydrochloride (0.0015 N : 0.0030 N) -- (eluent solution for divalent cations) Add 1.087 g of mPDA 2HCl and 0.50 mL of concentrated HCl to about 500 mL of water (Sect. 7.2). Mix well and dilute to 4 L with water (Sect. 7.2).

7.4 HYDROCHLORIC ACID (1.0 N) -- Add 83.0 mL of concentrated HCl (sp gr 1.19) to 900 mL of water (Sect. 7.2) and dilute to 1 L.

7.5 REGENERATION SOLUTION -- Prepare the following solutions for use with packed bed, fiber, or micromembrane suppressors.

7.5.1 Sodium Hydroxide (0.5 N) -- (regenerant for a packed bed column) Dissolve 80 g of sodium hydroxide (NaOH) in water (Sect. 7.2) and dilute to 4 L.

7.5.2 Tetramethylammonium hydroxide (0.04 N) -- (regenerant for a fiber or micro-membrane suppressor) Dissolve 29.976 g of tetramethylammonium hydroxide pentahydrate (TMAOH $5H_2O$) in water (Sect. 7.2) and dilute to 4 L. Alternatively, add 58.4 mL of a 25% solution of TMAOH to water (Sect. 7.2) and dilute to 4 L.

7.5.3 Barium Hydroxide (0.08 N) -- (regenerant for a fiber or micro-membrane suppressor) Dissolve 50.45 g of barium hydroxide octahydrate ($Ba(OH)_2$ $8H_2O$) in water (Sect. 7.2) and dilute to 4 L. Carbon dioxide present in the air and water will form barium carbonate ($BaCO_3$) that must be filtered out of the regenerant before it enters the micro-membrane suppressor. To prevent the intake of $BaCO_3$ precipitate into the suppressor, install a filter over the inlet end of the regenerant line. Agitate the regenerant thoroughly before use to ensure that the barium hydroxide is completely in solution.

7.6 STOCK STANDARD SOLUTIONS -- Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials as listed below. Store the solutions at room temperature in high density polyethylene or polypropylene containers.

7.6.1 Ammonium Solution, Stock (1.0 mL = 1.0 mg NH_4) -- Dissolve 2.9654 g of ammonium chloride (NH_4Cl), dried at 105°C for 1 hour, in water (Sect. 7.2) and dilute to 1 L.

7.6.2 Calcium Solution, Stock (1.0 mL = 1.0 mg Ca) -- Add 2.497 g of calcium carbonate ($CaCO_3$), dried at 180 °C for one hour, to approximately 600 mL of water (Sect. 7.2). Add concentrated hydrochloric acid (HCl, sp gr 1.19) slowly until all the solid has dissolved. Dilute to 1 L with water (Sect. 7.2).

7.6.3 Magnesium Solution, Stock (1.0 mL = 1.0 mg Mg) -- Dissolve 1.000 g of magnesium ribbon in a minimal volume of 6 N HCl and dilute to 1 L with water (Sect. 7.2).

7.6.4 Potassium Solution, Stock (1.0 mL = 1.0 mg K) -- Dissolve 1.9067 g of potassium chloride (KCl), dried at 105°C for 1 hour, in water (Sect. 7.2) and dilute to 1 L.

7.6.5 Sodium Solution, Stock (1.0 mL = 1.0 mg Na) -- Dissolve 2.5420 g of sodium chloride (NaCl), dried at 105°C for 1 hour, in water (Sect. 7.2) and dilute to 1 L.

7.7 SAMPLE CONTAINERS -- Use polyolefin or glass sample holders that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The dissolution of particulate materials and the presence of microbial activity will affect the stability of all of the cations in this method. This instability generally results in increased concentrations of magnesium, calcium, sodium, and potassium and decreased ammonium concentrations. Ion chromatographic measurements should be made immediately after sample collection when possible. Refrigeration of samples at 4°C will retard but not prevent changes in the concentration of these species (14.5).

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is effective at stabilizing magnesium, calcium, sodium, and potassium concentrations that are influenced by the dissolution of alkaline particulate matter (14.5). Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus. Filtered samples are stable for a period of six weeks.

8.3.2 Filtration followed by refrigeration at 4°C is the recommended preservation technique for ammonium ion. Holding times should not exceed seven days.

9. CALIBRATION AND STANDARDIZATION

9.1 Assemble the ion chromatograph according to the manufacturer's instructions. Recommended operating conditions for the apparatus are listed in Table 1. Included in Table 2 are retention times characteristic of this method. Other columns, chromatographic conditions, or detectors may be used provided the requirements in Sect. 6 are met.

9.2 Bring all standards, samples, eluents, and regenerants to ambient temperature before beginning any analyses. Maintain laboratory temperature conditions within ±3°C while conducting analyses.

9.3 Use the eluent strength in Sect. 7.3 for wet deposition analyses. If peak resolution is not adequate, it may be necessary to decrease the eluent strength. Refer to the manufacturer's recommendations for guidelines on optimizing eluent strength.

9.4 Adjust the instrument flow rate for optimal peak resolution. Decreasing the flow rate may provide greater peak resolution but will lengthen retention times. Increasing the flow rate decreases peak resolution and shortens retention times. Refer to the manufacturer's recommendations for guidelines on optimizing flow rate.

9.5 Equilibrate the system by pumping eluent through all the columns and the detector until a stable baseline is obtained.

9.6 CALIBRATION SOLUTIONS

9.6.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain the analyte(s) of interest at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of the analyte in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. If a second detector sensitivity scale setting is used to increase the instrument's concentration range, calibrate at the two sensitivity levels. Suggested calibration standards for each analyte are listed in Table 2.

9.6.2 Prepare all calibration standards by diluting the stock standards (Sect. 7.6). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The calibration standards are stable for one week when stored at 4°C in high density polyethylene containers.

9.6.3 Sodium, ammonium, potassium, magnesium, and calcium can be combined into a single solution at each of the five standard concentration levels.

9.7 CALIBRATION CURVE

9.7.1 Flush the sampling system with the calibration standard using at least ten times the injection loop volume. Inject the standard and record the peak height or area response. Repeat this procedure for the remaining standards. Construct calibration curves for each of the five analytes according to Sect. 12.

9.7.2 Record the retention times for each analyte. Measure retention time from an initial starting point on the chromatogram.

9.7.3 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.5.

9.7.4 Whenever a new eluent or regenerant solution is made, reestablish the calibration curve.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.6). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.4 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 4. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.7), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the concentrations of the cations of interest. If the solution concentrations exceed the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample after the ion chromatograph has been calibrated. This sample may be formulated in the laboratory, or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the ion chromatograph or calibration curve. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any biases introduced in the field and laboratory handling procedures. the data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.6). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Check the instrumental operating parameters each day according to Sect. 9 and Table 1.

11.2 Prepare all standards and construct calibration curves according to Sect. 9.6 and 9.7.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.4 SAMPLE INJECTION

11.4.1 Use the same size injection loop for both standards and samples. Samples may be injected manually with a syringe or with an autosampler.

11.4.2 Flush the sampling system thoroughly with each new sample using a rinse volume of at least ten times the loop size. Inject the sample, avoiding the introduction of air bubbles into the system.

11.4.3 Record the resulting peak heights or areas.

11.5 If the peak height or area response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.6 Sample chromatograms are provided in Figures 2 and 3.

12. CALCULATIONS

12.1 For each analyte of interest, calculate a linear least squares fit of the standard concentrations as a function of the measured peak height or area. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in mg/L
x = peak height or area measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of peak height or area measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of analyte of interest from the calibration curve.

12.2 If the relationship between standard concentration and measured peak height or area is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2 x^2 + B_1 x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of analyte of interest from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of the analyte of interest.

12.4 Report data in mg/L as Na^+, NH_4^+, K^+, Mg^{+2}, and Ca^{+2}. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.7). The results are summarized in Table 3. No statistically significant biases were found for any of the five inorganic cations.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 4.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Definitions of Terms Related to Water," Standard D 1129-82b, 1982, p. 4.

14.2 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.3 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.4 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.5 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. **12**, 1978, pp. 2343-2349.

14.6 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.7 Annual Book of ASTM Standards, Section 11, **Vol. 11.01 (1)**, "Practice for Interlaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Method Detection Limits and Concentration Ranges for Chemically Suppressed Ion Chromatographic Determination of Cations in Wet Deposition.

Analyte	Method Detection Limit,[a] mg/L	Concentration Range, mg/L
Sodium	0.03	0.03 - 1.00
Ammonium (as NH_4^+)	0.03	0.03 - 2.00
Potassium	0.01	0.01 - 1.00
Magnesium	0.02	0.02 - 1.00
Calcium	0.02	0.02 - 3.00

a. Chromatographic Conditions:
- Guard Column -- Dionex CG1
- Separator Column -- Dionex CS1
- Fiber Suppressor Column -- Dionex CFS
- Detector -- As specified in 6.1.5
- Eluent -- As specified in 7.3
- Sample Loop -- 100 uL
- Flow Rate -- 2.3 mL/min
- Detector Sensitivity -- 10 uS/cm

Table 2. Retention Times and Suggested Calibration Standard Concentrations for the Determination of Cations in Wet Deposition.[a]

Analyte	Approximate Retention Time Range,[b] sec	Calibration Standards, mg/L
Sodium	276 - 336	zero 0.03 0.25 0.50 0.75 1.00
Ammonium (as NH_4^+)	432 - 512	zero 0.03 0.25 0.50 0.75 1.00
Potassium	528 - 636	zero 0.01 0.05 0.10 0.20 0.25
Magnesium	144 - 204	zero 0.02 0.10 0.15 0.20 0.30
Calcium	252 - 324	zero 0.02 0.40 0.75 1.10 1.50

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a. Based on the MDL and 95th percentile concentrations of each analyte obtained from analyses of over five thousand wet deposition samples from the NADP/NTN precipitation network.

b. The retention time was measured from the time of injection. For chromatographic conditions, refer to Table 1.

Table 3. Single-Operator Precision and Bias for Sodium, Ammonium, Potassium, Magnesium, and Calcium Determined from Analyte Spikes of Wet Deposition Samples.[a]

Analyte	Amount Added, mg/L	n[b]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[c]
Sodium	0.108	10	95.3	-0.001	0.010	No
	0.273	9	94.4	-0.015	0.010	No
Ammonium	0.188	10	113.8	0.026	0.030	No
	0.473	9	107.5	0.035	0.025	No
Potassium	0.014	8	157.1	0.008	0.009	No
	0.034	8	132.4	0.011	0.016	No
Magnesium	0.018	9	89.5	-0.002	0.004	No
	0.044	9	92.3	-0.003	0.002	No
Calcium	0.079	10	93.9	-0.005	0.008	No
	0.199	10	97.1	-0.008	0.014	No

---

a. Concentrations are significant to two decimal places. For chromatographic conditions, refer to Table 1.

b. Number of replicates

c. 95% Confidence Level

Table 4. Single-Operator Precision and Bias for Sodium, Ammonium, Potassium, Magnesium, and Calcium Determined from Quality Control Check Samples.[a]

Analyte	Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[b]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
Sodium	0.082	0.090	7	0.008	9.8	0.009	10.0
	0.465	0.454	7	-0.011	-2.4	0.019	4.2
Ammonium	0.063	0.067	7	0.004	6.4	0.011	16.4
	0.400	0.400	7	0.000	0.0	0.032	8.0
Potassium	0.021	0.024	7	0.003	14.3	0.004	16.7
	0.098	0.098	7	0.000	0.0	0.005	5.1
Magnesium	0.018	0.026	7	0.008	44.4	0.008	30.8
	0.084	0.085	7	0.001	1.2	0.018	21.2
Calcium	0.053	0.058	7	0.005	9.4	0.006	10.3
	0.406	0.405	7	-0.001	-0.2	0.045	11.1

---

a. Concentrations are significant to two decimal places. For chromatographic conditions, refer to Table 1.

b. Number of replicates.

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Sodium, Ammonium, Potassium, Magnesium, and Calcium.

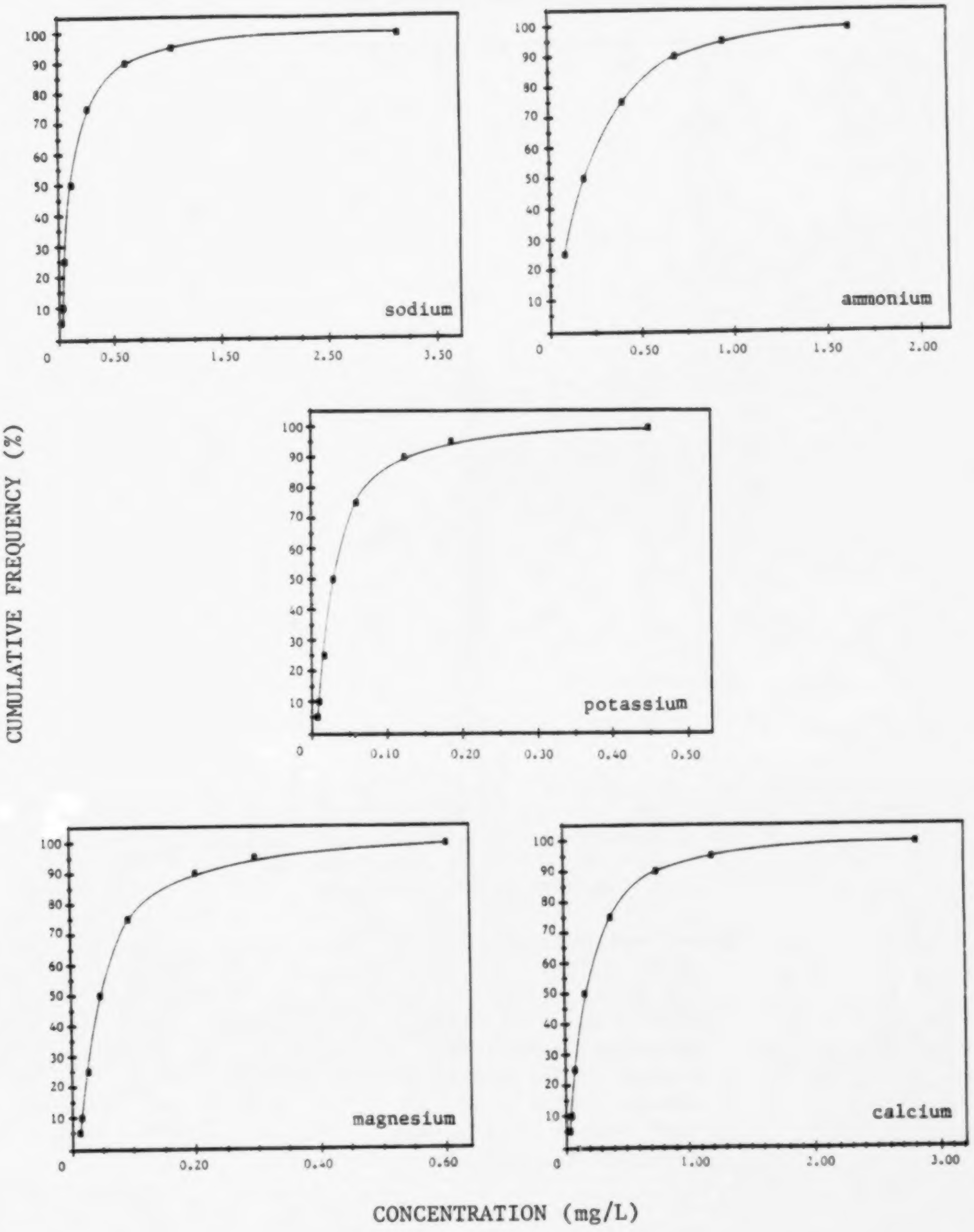
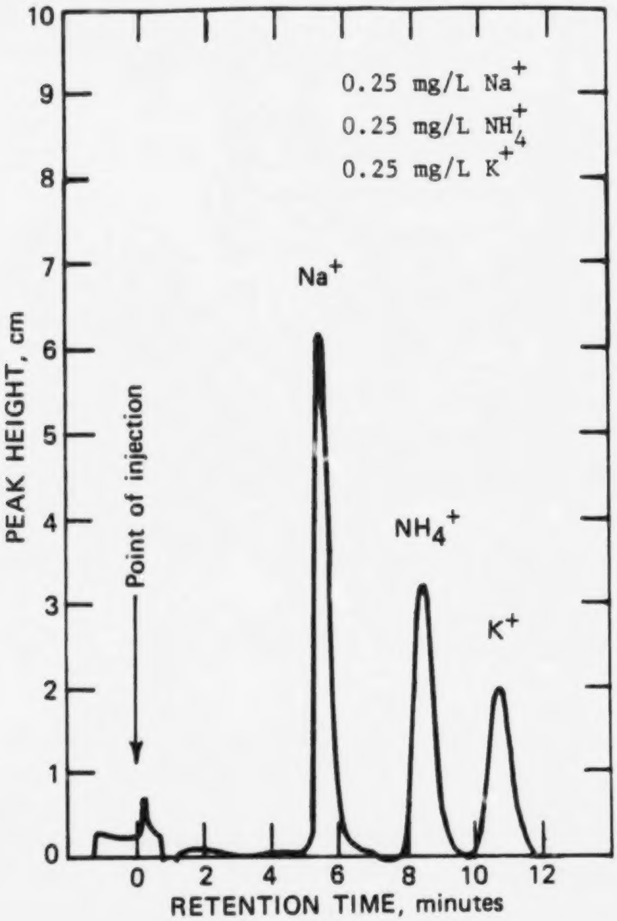


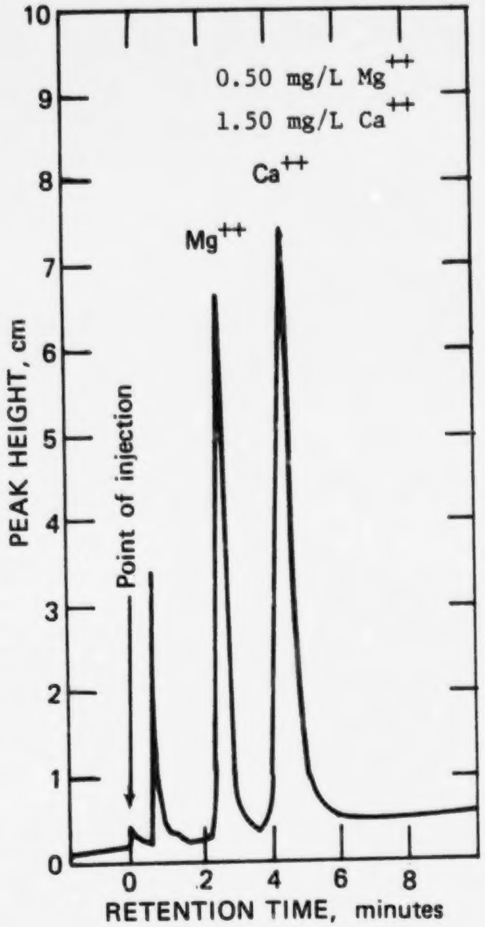
Figure 2. Chromatogram of a Calibration Standard Containing Sodium, Ammonium, and Potassium.



Chromatographic Conditions:

- Guard Column -- Dionex CG1
- Separator Column -- Dionex CS1
- Fiber Suppressor Column -- Dionex CFS
- Detector -- As specified in 6.1.5
- Eluent -- As specified in 7.3
- Sample Loop -- 100 μL
- Flow Rate -- 2.3 mL/min
- Detector Sensitivity -- 10 μS/cm

Figure 3. Chromatogram of a Calibration Standard Containing Magnesium and Calcium.



Chromatographic Conditions:
- Guard Column -- Dionex CG1
- Separator Column -- Dionex CS1
- Fiber Suppressor Column -- Dionex CFS
- Detector -- As specified in 6.1.5
- Eluent -- As specified in 7.3
- Sample Loop -- 100 µL
- Flow Rate -- 2.3 mL/min
- Detector Sensitivity -- 10 µS/cm

Method 305.6 -- Acidity in Wet Deposition by Titrimetric Determination

March 1986

Performing Laboratory:

Jacqueline M. Lockard
Kenni O. James
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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1. Sample Vessel Used for an Acidity Titration.
2. A Standard Titration Curve with Gran's Plot for an Equimolar Mixture of Dilute Nitric Acid and Acetic Acid.
3. A Standard Titration Curve with Gran's Plot for a Dilute Nitric Acid Solution.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the titrimetric determination of strong and total acidity by electrometric measurement using either a pH half cell with a reference probe or a combination electrode as the sensor. The concentration of weak acids present is determined from the difference between the measured total and strong acidities. These guidelines outline the procedure by which titration to an end point pH is to be made on wet deposition samples.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a 5.0×10^{-5} N nitric acid solution is 5 ueq/L.

2. SUMMARY OF METHOD

2.1 The pH meter and the associated electrode(s) are calibrated against two reference buffer solutions that bracket the anticipated sample pH. Small increments of a sodium hydroxide solution are added to an unfiltered wet deposition sample. The course of the titration is followed by measuring the pH and the amount of titrant added as the titration progresses to a pH of 10.3. The strong acid equivalence point lies at the inflection point of the curve, i.e., at the point of maximum slope. The presence of dissociated weak acids in the sample will make the accurate determination of this equivalence point difficult. To reduce the potential for error when graphically determining the equivalence point, a method developed by Gran (14.1) is used. A plot of Gran's function versus volume of titrant added to the sample is constructed, from which strong, weak, and total acidities are derived.

DEFINITIONS

3.1 pH -- the negative logarithm to the base ten of the conventional hydrogen ion activity (14.2):

$$pH = -\log[H^+]$$

3.2 ACIDITY -- the quantitative capacity of aqueous media to react with hydroxyl ions.

3.3 TITRATION -- a method for determining the concentration of a dissolved substance in terms of the amount of a reagent of known concentration required to quantitatively react with a measured volume of the test solution.

3.4 EQUIVALENCE POINT -- the point in the process of a titration at which the titrated species and titrant are present in equivalent amounts.

3.5 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.3).

4. INTERFERENCES

4.1 The pH meter and the associated electrode(s) reliably measure pH in nearly all aqueous solutions and in general are not subject to solution interference from color, turbidity, oxidants, or reductants.

4.2 The true pH of an aqueous solution is affected by the temperature. The electromotive force between the glass and the reference electrode is a function of temperature as well as pH. Temperature effects caused by a change in electrode output can be compensated for automatically or manually depending on the pH meter selected.

4.3 Organic humic materials present in wet deposition samples degrade the glass electrode performance by coating the sensing bulb. Difficulty encountered when standardizing the electrode(s), erratic readings, or slow response times may be an indication of contamination of the glass bulb. To remove these coatings, refer to the manual accompanying the probe for the manufacturer's recommendations.

4.4 As discussed in Sect. 4.5 of Method 150.6 of this manual, measuring pH in solutions while stirring can result in errors due to residual streaming potentials. These errors are minimized by maintaining a constant stirring rate during both meter calibration and sample titration. The effect of streaming potentials is less important during titrimetric procedures since the relative, and not the absolute, change in pH values with added titrant is used to calculate acidity. Stirring the sample throughout the titration ensures complete mixing of titrant and sample and reduces the time necessary to complete the procedure.

Note: When magnetic stirring is used, avoid sample contamination when inserting the stirring bar. Maintain an air space between the surface of the stirring motor and the sample container to prevent heating the sample.

4.5 Dissolved gases affecting sample acidity, such as carbon dioxide or ammonia, may be gained or lost during sampling, storage, or titration. Minimize these effects by titrating to the end point promptly after opening the sample container. Purge the sample of CO_2 with a nitrogen stream and maintain a nitrogen atmosphere within the vessel throughout the titration.

4.6 The important assumption in Gran's method is that only strong acids contribute to the free acidity of a solution. The presence of weak acids (formic acid, acetic acid, and the ammonium ion) and hydrolyzable metal salts ($Al(H_2O)_6$) can lead to an overestimate of both the strong and the total acidity when using this technique. In the absence of complete chemical characterization of the wet deposition sample to correct for this overestimation, the usefulness of the data obtained by this method becomes limited (14.4).

5. SAFETY

5.1 The reference buffer solutions, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated nitric acid (Sect. 7.6) and sodium hydroxide (Sect. 7.8).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.5).

6. APPARATUS AND EQUIPMENT

6.1 LABORATORY pH METER -- The meter may have either an analog or digital display but must have a 0.01 pH unit sensitivity. A meter that has separate calibration and slope adjustment features and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be powered by battery or 110 VAC; if battery powered, the meter must have a battery check feature. A temperature compensator control to allow accurate measurements at temperatures other than 25°C is desirable.

6.2 SENSING ELECTRODE -- Select a sensing electrode constructed of general purpose glass. This electrode type generates lower resistance, faster response, and has a reliable range of 0-14 pH units. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

6.3 REFERENCE ELECTRODE -- Select a reference probe compatible with the sensing electrode used. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

6.4 COMBINATION ELECTRODE -- The combination electrode combines the indicating and reference elements in a single unit. Since sample volume requirements are a consideration when analyzing wet deposition samples, combination electrodes are more convenient than separate glass and reference electrodes. Refer to the manual accompanying the probe for the manufacturer's recommendations on electrode storage.

6.5 TEMPERATURE CONTROL -- To ensure accurate results, use either a constant temperature water bath, a temperature compensator, or a thermometer to verify that all standards and samples are maintained at temperatures within ±1°C of one another. If a thermometer is used, select one capable of being read to the nearest 1°C and covering the range 0° to 40°C.

6.6 MICROBURET -- For the addition of titrant, select a microburet or an autoburet assembly. Alternatively, a micropipette capable of reproducibly delivering 5 uL of solution may be used.

6.7 STIRRING DEVICE -- electric or water-driven. If an electric stirrer is selected, leave an air gap or place an insulating pad between the stirrer surface and the solution container to minimize heating of the sample. Use a TFE-fluorocarbon-coated stirring bar.

6.8 TITRATION VESSEL -- Use a borosilicate glass or polyolefin vessel with a 75-mL capacity. Equip the vessel with a lid having openings to accommodate the pH electrode(s), a nitrogen purge line, buret, and exhaust (to prevent pressure build-up as N_2 is pumped into the chamber). A suitable titration vessel is illustrated in Figure 1.

6.9 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS) where such specifications are available.

7.2 PURITY OF WATER -- Use carbon dioxide-free water prepared by boiling ASTM Type II water (14.6) in a conical flask for 20 minutes. Stopper the flask with a 1-hole rubber stopper fitted to a soda lime-ascarite drying tube and allow the water to cool. Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 NITROGEN, GAS -- Use pre-purified nitrogen gas (N_2, 99.995%) to purge the sample of carbon dioxide and maintain a N_2 atmosphere above the sample during titration.

7.4 POTASSIUM HYDROGEN PHTHALATE SOLUTION (0.02 N) -- Dissolve 4.00 g of potassium hydrogen phthalate ($KHC_8H_4O_4$), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L.

7.5 QUALITY CONTROL CHECK SAMPLES (QCS) -- Prepare the following solutions and analyze according to Sect. 11.3-11.4 to verify the titration procedure.

7.5.1 Strong Acid -- Nitric Acid (5.0×10^{-5} N) -- Dilute 1.0 mL of concentrated nitric acid (HNO_3, sp gr 1.42) to 1 L with water (Sect. 7.2). Dilute 3.2 mL of this stock solution to 1 L with water (Sect. 7.2). The resulting solution has a pH of 4.30 ± 0.10 and a total acidity of 50.1 ± 10.0 ueq/L at 25°C. Store at room temperature in a high density polyethylene or polypropylene container.

7.5.2 Mixed Strong/Weak Acid -- Nitric Acid : Acetic Acid (2.5×10^{-5} N : 2.5×10^{-5} N) -- Dilute 1.0 mL of concentrated nitric acid to 1 L with water (Sect. 7.2). Dilute 1.0 mL of concentrated acetic acid ($HC_2H_3O_2$, sp gr 1.05) to 1 L with water (Sect. 7.2). Combine 1.60 mL of HNO_3 solution with 1.45 mL of $HC_2H_3O_2$ solution and dilute to 1 L with water (Sect. 7.2). The resulting solution has a pH of 4.60 ± 0.10 and a total acidity of 50.6 ± 5.0 ueq/L at 25°C. Store at room temperature in a high density polyethylene or polypropylene container.

7.6 REFERENCE BUFFER SOLUTIONS -- Table 1 identifies each buffer salt by its National Bureau of Standard (NBS) number and provides a recommended drying procedure prior to use. Store the reference buffer solutions in polyethylene or chemical-resistant glass bottles and replace yearly or sooner if a visible change such as the development of colloidal or particulate materials is observed.

7.6.1 Phthalate Reference Buffer Solution (0.02 N HCl, 0.05 N $KHC_8H_4O_4$) -- Add 83.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to water (Sect. 7.2) and dilute to 1 L. Dissolve 10.20 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in 22.3 mL of the hydrochloric acid solution and dilute to 1 L with water (Sect. 7.2). This solution has a pH of 3.00 at 25°C.

7.6.2 Phthalate Reference Buffer Solution (0.05 N $KHC_8H_4O_4$) -- Dissolve 10.12 g of potassium hydrogen phthalate ($KHC_8H_4O_4$) in water (Sect. 7.2) and dilute to 1 L. This solution has a pH of 4.00 at 25°C.

7.6.3 Phosphate Reference Buffer Solution (0.005 N NaOH, 0.05 N KH_2PO_4) -- Dissolve 4.00 g of sodium hydroxide (NaOH) in water (Sect. 7.2) and dilute to 1 L. Dissolve 6.80 g of potassium dihydrogen phosphate (KH_2PO_4) in 56.0 mL of the hydroxide solution and dilute to 1 L with water (Sect. 7.2). This solution has a pH of 6.00 at 25°C.

7.6.4 Phosphate Reference Buffer Solution (0.03 N NaOH, 0.05 N KH_2PO_4) -- Dissolve 40.0 g of sodium hydroxide (NaOH) in water (Sect. 7.2) and dilute to 1 L. Dissolve 6.80 g of potassium dihydrogen phosphate (KH_2PO_4) in 29.1 mL of the hydroxide solution and dilute to 1 L with water (Sect. 7.2). This solution has a pH of 7.00 at 25°C.

7.6.5 Commercial Buffer Solutions -- Commercially available buffer solutions traceable to NBS buffers are adequate for standardization. These buffer solutions have pH values near 3, 4, 6, or 7. The exact pH and use temperature are provided by the supplier of the specific buffer.

7.7 SODIUM HYDROXIDE SOLUTION, TITRANT (0.02 N) -- Use commercially available 0.02 N sodium hydroxide solution or prepare from ACS reagent grade materials. Dissolve 1.0 g of sodium hydroxide (NaOH) in 10 mL of water (Sect. 7.2), cool, and filter through hardened filter paper. Dilute the filtrate to 1 L with water (Sect. 7.2). Standardize with potassium hydrogen phthalate (Sect. 7.5) according to Sect. 9.2. Calculate the normality using the equation in Sect. 12.2. Refrigerate the solution at 4°C in a high density polyethylene or polypropylene container.

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from sequential sampling within a wet deposition event to total event samples. In addition to the replacement of sampling containers at the cessation of each wet deposition event, a routine weekly container change is recommended. This replacement protocol ensures sample integrity which may be compromised by long term container exposure.

8.3 The dissolution of particulate materials and the presence of microbial activity will affect the stability of both the strong and the weak acid components of wet deposition samples (14.7, 14.8). This instability generally results in a decrease in measured acidity. Titrations should be made immediately after sample collection and thermal equilibration with calibration buffers. Refrigeration of samples at 4°C will minimize but not prevent a decrease in the hydrogen ion content.

8.3.1 Filtration of samples through a deionized water leached 0.45 micrometer membrane is effective at stabilizing the acidic components of the wet deposition sample that are influenced by the dissolution of alkaline particulate matter (14.7). Monitoring of the filtration procedure is necessary to ensure that sample acidities are not affected by the membrane or filtration apparatus.

8.3.2 A biocide such as chloroform ($CHCl_3$) may be used to stabilize the organic acid component of the sample and to prevent changes in acid content due to biological actions on other sample constituents (14.8). Add the chloroform (0.5 mL per 250 mL sample) to a separate sample aliquot that will be used only for the determination of strong and total acid components.

9. CALIBRATION AND STANDARDIZATION

9.1 Turn on the meter and allow it to warm up according to manufacturer's instructions.

9.2 If necessary, add filling solution to the electrode before using. Maintain the filling solution level at least one inch above the level of the sample surface to ensure proper electrolyte flow rate.

9.3 Determine the temperature of the wet deposition sample. Allow sample, buffers, and QCS solutions to reach room temperature (±1°C) before using for calibration or titration.

9.4 Select two reference buffer solutions that bracket the anticipated pH of the wet deposition sample. The difference between the nominal pH of each buffer solution should not exceed three units. A pH 7.00 and a pH 4.00 buffer are most frequently used for wet deposition studies.

9.5 CALIBRATION FUNCTION

9.5.1 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Dispense 20-40 mL of the buffer with the higher pH into the titration vessel (Fig. 1). Insert the stirring bar and continue stirring throughout the calibration procedure at a rate of 4 revolutions per second (rps). Maintain a nitrogen atmosphere within the titration chamber during measurement as in Sect. 11.4.1.

9.5.2 Insert the electrode(s) into the buffer and allow time for the reading to remain stable within ±0.01 pH units over a 30 second period.

9.5.3 Adjust the calibration function until the reading corresponds to the temperature corrected value of the reference buffer solution.

9.6 SLOPE FUNCTION

9.6.1 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Dispense 20-40 mL of the second reference buffer solution into the titration vessel. Insert the stirring bar and continue stirring throughout the calibration procedure. Maintain a nitrogen atmosphere within the titration chamber during measurement as in Sect. 11.4.1.

9.6.2 Insert the electrode(s) into the buffer and allow the system to equilibrate as directed in Sect. 9.5.2.

9.6.3 Adjust the slope function until the reading corresponds to the temperature corrected value of the second reference buffer solution.

9.7 CALIBRATION CHECK

9.7.1 Remove the electrode(s), rinse thoroughly, and place into the first reference buffer solution following the procedure in Sect. 9.5. If the pH does not read within ±0.01 units of the temperature corrected value, repeat the calibration procedure until the buffers agree.

9.8 To standardize the NaOH titrant prepared in Sect. 7.8, fill a 25-mL buret with 0.02 N $KHC_8H_4O_4$ (Sect. 7.5). Pipette 20 mL of 0.02 N NaOH into a beaker and immerse a calibrated pH electrode into the solution. Add $KHC_8H_4O_4$ solution to the dilute NaOH in small increments until the pH of the solution reads 8.70. Calculate the normality of the NaOH using the equation provided in Sect. 12.2.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.9). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor the analyses of quality control check samples (QCS).

10.2.1 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) for the measured acidity of each QCS titrated. Use the certified or NBS traceable acidity as the mean (target) value ($\overline{x}$). A warning limit of $\overline{x} \pm 2s$ and a control limit of $\overline{x} \pm 3s$ should be used. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. If the measured acidity found by titration of the QCS solution falls outside of the $\pm 3s$ limits, recalibrate the system and reanalyze all samples from the last time the system was in control. If two successive QCS acidity measurements are outside of the $\pm 2s$ limits, verify the meter calibration according to Sect. 10.5 before continuing with titrations. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 2. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.2 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the solution pH. If the measured pH is not within the range of 5.4-6.0, a contamination problem is indicated in the cleaning procedure. Corrective action should be taken before the sampling containers are used for the collection of wet deposition.

10.4 Electrodes used for the measurement of wet deposition samples should not be used for other sample types. Strongly acidic or basic solutions may cause electrode degradation and result in biased measurements and/or slow response in wet deposition samples. Similarly, samples characterized by high concentrations of organic matter may leave a residue on the glass sensing bulb resulting in slow electrode response.

10.5 Verify the meter calibration after every ten samples and at the end of each day's analyses using both reference buffer solutions. The pH measured for the calibration buffers must agree within ±0.02 of the nominal value reported for each buffer. If the measured pH of either buffer falls outside of these limits, recalibrate the electrode/meter assembly and reanalyze those samples measured since the last time the system was in control.

10.6 Determine the pH and titrated acidity of a quality control check sample (QCS) after the meter and electrode assembly have been calibrated. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample selected must have a pH within the range of the calibration buffers and should approximate the acidity range of the samples to be analyzed. The use of two QCS samples, one a dilute strong acid solution and the other a dilute equimolar mixture of a strong and a weak acid, is recommended. If the measured acidity found by titration of the QCS is not within the specified limits of the control solution, recheck the meter calibration and recalibrate if necessary. Titrate a second aliquot. If acceptable results on the second aliquot cannot be obtained, systematically replace titrant, electrode, and then the meter. Titrate a separate aliquot of QCS after each change to determine if the problem was corrected. When the system is in control, titrate the QCS solutions as directed in Sect. 11. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.6.1 The pH and titrated acidity of the QCS should be measured at the start and completion of each batch of samples. If the QCS measurement is out of the predetermined control limits, check the calibration buffers and recalibrate if any one of the buffer values has shifted by more than 0.02 pH units. Recheck the QCS and reanalyze all samples from the last time the measurement system was in control.

10.7 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Bring all buffers and solutions to ambient temperature making sure any necessary compensation is made for deviations in temperature (Sect. 6.5).

11.2 Calibrate the electrode assembly with two reference buffer solutions as described in Sect. 9.1-7.

11.3 After the electrode(s) and meter are calibrated, titrate the QCS according to Sect. 11.4. If the pH and acidity measured for the QCS is not within the specified limits (Sect. 10.2.1), refer to Sect. 10.6.

11.4 SAMPLE ANALYSIS

11.4.1 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Pipette 20-40 mL of sample into the titration vessel. Record the volume of sample used and begin stirring the sample. Record the pH after the meter has stabilized to within ±0.01 units. Sparge the sample with N_2 for 10-15 minutes to remove dissolved CO_2. Raise the N_2 line to rest above the level of the solution to maintain a nitrogen atmosphere of ≤ 5 psi (3.5 g/m^2) within the titration chamber.

11.4.2 Record the pH of the sample after sparging. The difference in pH before and after sparging is a measure of the volatile weak acidity present. Carbon dioxide is the predominant volatile weak acid found in wet deposition samples. The contribution of dissolved CO_2 to lowering pH is generally negligible below pH 4.50. Add the 0.02 N NaOH titrant to the sample in increments of 1-10 uL. Determine the size of the increment of titrant added by the change in pH that results from each addition. When the change in pH is very small (<0.01), increase the volume of titrant added to 10 uL. Record both the volume of titrant added and the pH once the meter has become stable. Continue titrating the sample until a pH of approximately 10.4 is reached, recording pH and volume after each titrant addition.

11.4.3 Stir the sample throughout the titration. Rinse the titration assembly and vessel between each titration with at least three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle for a minimum of 30 seconds.

11.5 To perform the Gran's analysis on the results of the titration, refer to Sect. 12.3.

12. CALCULATIONS

12.1 Record pH measurements to the nearest hundredth of a pH unit and sample temperature to the nearest degree.

12.2 Calculate the normality (N) of the solutions standardized according to Sect. 9.9 as follows:

$$N = \frac{A \times B}{EW \times C} = \frac{4.0 \times B}{204.2 \times C} \quad eq/L$$

where: A = amount of $KHC_8H_4O_4$ in grams weighed into 1 L.
B = volume of $KHC_8H_4O_4$ used in titration in mL.
EW = equivalent weight of $KHC_8H_4O_4$ (204.2).
C = volume of NaOH titrated in mL.

12.3 To calculate total and strong acidity, a Gran's plot can be constructed using the volume and pH data from the titration. Calculate the Gran function for each point as follows (14.10):

$$\psi = (V_0 + V_T)10^{-pH_T}$$

$$\psi' = (V_0 + V_T)10^{pH_T}$$

where: ψ = Gran function before the equivalence point is reached
ψ' = Gran function after the equivalence point is reached
V_0 = initial volume of sample in mL
V_T = volume of titrant added in mL
pH_T = pH from meter corresponding to V_T

Plot the Gran function versus the volume of titrant (V_T). The curves ψ and ψ' vs. V_T are linear and intersect the V_T axis at V_E and V'_E, respectively. If significant weak acidity is present, the ψ function will be altered by the dissociation of the weak acids. This produces nonlinearity in the curve ψ vs. V_T. The linear portion of the curve can be extrapolated to obtain the equivalence point V_E for strong acidity. The intersection of the V_T axis of ψ'vs. V_T is the equivalence point for total acidity. See Figures 2 and 3.

$$\text{Strong acidity} = 10^{-6} C_B (V_E/V_0) \quad \text{ueq H}^+/\text{L}$$

$$\text{Total acidity} = 10^{-6} C_B (V'_E/V_0) \quad \text{ueq H}^+/\text{L}$$

where: C_B = Normality of titrant
V_E = volume of titrant added at the equivalence point in mL (strong acidity)
V'_E = volume of titrant added at the equivalence point in mL (total acidity)
V_0 = initial volume of sample in mL

The concentration of weak acid is obtained from the following relationship:

Weak Acidity = Total Acidity - Strong Acidity

13. PRECISION AND BIAS

13.1 Single-operator precision and bias data were obtained using two quality control check samples. The results are tabulated in Table 2.

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14.9 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985 U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.10 McQuaker, N. R., Kluckner, P. D. and Sandberg, D. K., "Chemical Analysis of Acid Precipitation: pH and Acidity Determinations," Environ. Sci. & Tech., **17**, 1983, pp. 431-435.

Table 1. National Bureau of Standards (NBS) Salts for Reference Buffer Solutions.

NBS Standard Sample Designation	Buffer Salt	Drying Procedure
186-1-c	potassium dihydrogen phosphate	2 h in oven at 130°C
185-f	potassium hydrogen phthalate	2 h in oven at 110°C

The buffer salts listed above can be purchased from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D. C. 20234.

Table 2. Single-Operator Bias and Precision from Acidity Titrations of Quality Control Check Samples.

Theoretical Total Acidity, ueq/L	Mean Measured Total Acidity, ueq/L	n[a]	Bias, ueq/L	Bias, %	Precision, s, ueq/L	Precision, RSD, %
50.1	50.1	10	0	0	1.8	3.6
50.5	47.8	7	-2.7	-5.4	2.4	5.0

The solutions used were a 5.01 x 10^{-5} N nitric acid solution (pH = 4.30) and a 5.05 x 10^{-5} N equimolar mixture of nitric acid and acetic acid (pH = 4.60).

a. Number of replicates

Figure 1. Sample Vessel Used for an Acidity Titration.

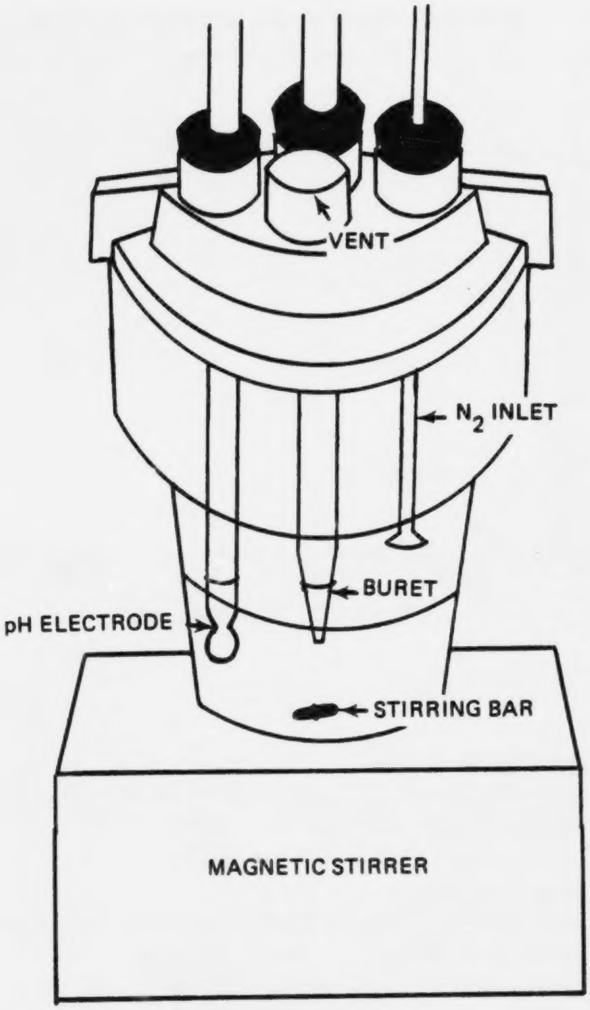
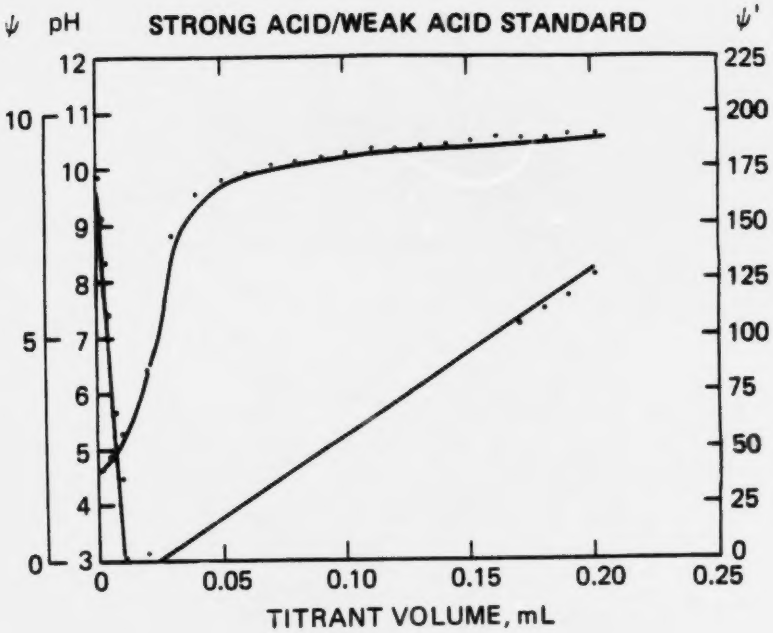

VENT
N_2 INLET
BURET
pH ELECTRODE
STIRRING BAR
MAGNETIC STIRRER

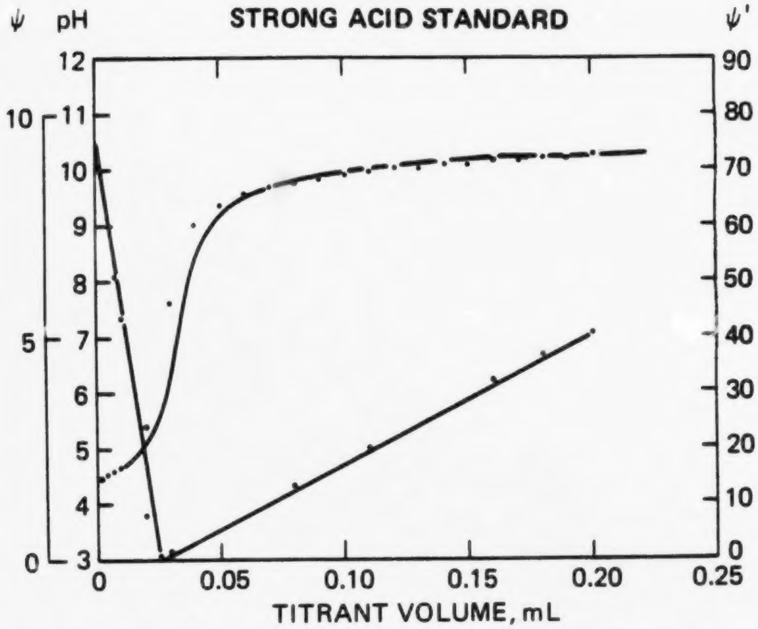
Figure 2. A Standard Titration Curve with Gran's Plot for an Equimolar Mixture of Dilute Nitric Acid and Acetic Acid.



Calculated Acidities
strong acidity = 25.3 μeq/L (pH = 4.60) = 50.1%
total acidity = 50.6 μeq/L = 100%
weak acidity = 25.2 μeq/L = 49.9%

Measured Acidities
mean strong acidity = 22.9 (±1.6) μeq/L (pH 4.64) = 47.9%
mean total acidity = 47.8 (±2.3) μeq/L
weak acidity = 24.9 μeq/L = 52.1%

Figure 3. A Standard Titration Curve with Gran's Plot for a Dilute Nitric Acid Solution.



Calculated Acidity

strong acidity = 50.4 μeq/L (pH 4.30) = 100%

Measured Acidities

mean strong acidity = 51.1 (±3.5) μeq/L (pH 4.29) = 99%

mean total acidity = 51.6 (±3.6) μeq/L

weak acidity = 0.5 μeq/L = 1%

Method 325.6 -- Chloride in Wet Deposition by Automated Colorimetric Determination Using Thiocyanate

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Performing Laboratory:

Brigita Demir
Susan R. Bachman
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Single-Operator Precision and Bias for Chloride Determined from Analyte Spikes of Wet Deposition Samples.
2. Single-Operator Precision and Bias for Chloride Determined from Quality Control Check Samples.

FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples: Chloride.
2. Chloride Sampling and Analytical System -- Segmented Flow.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the automated colorimetric determination of chloride in wet deposition samples by reaction with thiocyanate.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a calibration standard containing 0.10 mg/L chloride is 0.03 mg/L. The concentration range of this method is 0.03-2.00 mg/L as Cl^-.

1.4 Figure 1 represents a cumulative frequency percentile chloride concentration plot obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 A sample is mixed with a solution of saturated mercuric thiocyanate and ferric ammonium sulfate. Mercuric thiocyanate reacts with chloride ions in the sample to form mercuric chloride. The liberated thiocyanate ions then react with ferric ions to form a colored ferric thiocyanate complex. The intensity of the color of this complex is proportional to the concentration of chloride in solution. After color development, a flowcell receives the stream for measurement. A light beam of a wavelength characteristic of the ferric thiocyanate complex is passed through the solution. The light energy measured by photodetectors is a function of the concentration of chloride ion in the sample. Beer's Law is used to relate the measured transmittance to concentration:

$$\log(1/T) = abc$$

where: T = transmittance
a = absorptivity
b = length of light path
c = concentration of absorbing species (mg/L)

A calibration curve is constructed using standard solutions containing known concentrations of chloride. From this curve, the concentration of chloride in a wet deposition sample is determined.

3. DEFINITIONS

3.1 COLORIMETRY -- the measurement of light transmitted by a colored complex as a function of concentration.

3.2 For definitions of other terms used in these methods, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.1).

4. INTERFERENCES

4.1 Sample color absorbing in the wavelength range of 470-490 nm will increase the measured concentration of chloride in the sample. Wet deposition samples are generally colorless, therefore, this type of interference is rare.

4.2 Other halogens such as bromide and fluoride present in the sample will compete with chloride ions to complex the mercury from the mercuric thiocyanate reagent. The excess thiocyanate ions liberated form the colored ferric thiocyanate complex, resulting in an elevated concentration of chloride determined in the sample.

5. SAFETY

5.1 The calibration standards and sample types used in this method pose no hazard to the analyst. Many of the reagents, however, require special precautions as detailed below. Use a fume hood, protective clothing, and safety glasses when handling concentrated nitric (Sect. 7.4) and sulfuric acids (Sect. 7.7).

5.2 Use a fume hood and protective gloves when preparing the ferric ammonium sulfate solution (Sect. 7.4). Vapors produced by the reaction between ferric ammonium sulfate and nitric acid are hazardous.

5.3 Anytime the mercuric thiocyanate solution (Sect. 7.5) is prepared, wear gloves and avoid all skin contact with this poisonous reagent.

CAUTION: When discarding the mercuric sulfide waste, follow the precautions detailed in Sect. 11.7.

5.4 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.2).

6. APPARATUS AND EQUIPMENT

6.1 AUTOMATED COLORIMETRIC INSTRUMENT -- Select and assemble an analytical system consisting of the following:

6.1.1 Sampler.

6.1.2 Proportioning Pump.

6.1.3 Analytical Cartridge.

6.1.4 Colorimeter with a 480 nm wavelength setting. Ensure that the colorimeter is equipped with photodetectors having maximum sensitivity at this wavelength setting. A 15 mm flow cell is adequate to achieve the MDL stated in Sect. 1.3.

6.1.5 Strip Chart Recorder (or other data acquisition device).

6.1.6 Printer (optional).

6.2 Wherever possible, use glass transmission lines with an inside diameter of 1.86 mm (0.073 inches) in the analytical cartridge and colorimeter. Glass yields a more uniform sample flow and does not degrade as quickly as other tubing materials. When connecting two glass lines, ensure that the ends are abutted. To minimize pulsing of the analytical stream, maintain uniform inside diameter throughout all transmission tubing. Minimize the length of all transmission tubing to optimize the performance of the hydraulic system.

6.3 Enclose the sampler with a dust cover to prevent contamination.

6.4 To prevent the intake of any precipitates from the reagents, install intake filters at the end of the transmission lines that are used to transport the reagents from their respective containers to the proportioning pump.

6.5 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.3). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 CHLORIDE SOLUTION, STOCK (1.0 mL = 1.0 mg Cl) -- Dissolve 1.6485 g of sodium chloride (NaCl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container.

7.4 FERRIC AMMONIUM SULFATE SOLUTION -- Dissolve 60 g of ferric ammonium sulfate ($FeNH_4(SO_4)_2 \cdot 12(H_2O)$ in approximately 500 mL of water (Sect. 7.2). Add 355 mL of concentrated nitric acid (HNO_3, sp gr 1.42) and dilute to 1 L with water (Sect. 7.2). Filter the solution and add 0.5 mL Brij-35 or a similar wetting agent. This solution is stable for one year when stored at room temperature in an amber glass container.

CAUTION: The vapors produced when ferric ammonium sulfate is dissolved in acid are hazardous. Refer to Sect. 5.2 for an explanation of necessary safety precautions.

7.5 MERCURIC THIOCYANATE SOLUTION (Saturated) -- Add 5 g of mercuric thiocyanate ($Hg(SCN)_2$) to water (Sect. 7.2) and dilute to 1 L. Decant and filter a 200 mL portion of the saturated supernatant liquid to use as the reagent. Store the solution at room temperature in a high density polyethylene or polypropylene container.

CAUTION: Mercuric thiocyanate solution is a poisonous reagent. Avoid all skin contact with this solution. Refer to Sect. 5.3 for an explanation of necessary safety precautions.

7.6 SAMPLER RINSE WATER -- Add 0.5 mL Brij-35 or another suitable wetting agent to 1 L of water (Sect. 7.2).

7.7 SULFURIC ACID (7.2 N) -- Add 200 mL of sulfuric acid (H_2SO_4, sp gr 1.84) to water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a glass container.

7.8 THIOACETAMIDE SOLUTION (13% w/v) -- Dissolve 130 g of thioacetamide (CH_3SCNH_2) in water (Sect. 7.2) and dilute to 1 L. This solution is stable for one year when stored at room temperature in a glass container.

7.9 SAMPLE CONTAINERS -- Use polyolefin sample cups or glass test tubes that have been thoroughly rinsed with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 Chloride ion has been found to be stable in HDPE bottles for six weeks without special preservation techniques such as filtration or refrigeration (14.4).

9. CALIBRATION AND STANDARDIZATION

9.1 INSTRUMENT OPTIMIZATION

9.1.1 For a flow segmented system with a concentration range from 0.03-2.00 mg/L as chloride, assemble the sampling and analytical system as shown in Figure 2.

9.1.2 Use flow rated polyvinyl chloride (PVC) or polyethylene pump and transmission tubing throughout the sampling and analytical system. Use polyethylene tubing to transport the ferric ammonium sulfate reagent. This solution will degrade PVC tubing quickly. Check the tubing for chemical buildup, splits, cracks, and deformations before beginning each day's analysis. Change pump tubes after 50 hours of operation. Change transmission tubing after 100 hours of operation or when uneven flow patterns are observed. Replace the tubing used to transport the ferric ammonium sulfate reagent daily.

9.1.3 Optimize the tension of the pump tubes according to manufacturer's recommendations.

9.1.4 Set the wavelength of the colorimeter to 480 nm. Allow the colorimeter to warm up for 30 minutes while pumping sampler rinse water (Sect. 7.6) and reagents through the system. After a stable baseline has been obtained, adjust the recorder to maximize the full-scale response.

9.1.5 Sample at a rate of 40 samples/hour with a 1:4 sample to rinse ratio. This sampling rate provides good peak separation. Adjust the colorimeter to maximize sensitivity while minimizing instrument noise. Refer to the manufacturer's recommendations.

9.2 CALIBRATION SOLUTIONS

9.2.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain chloride at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of chloride in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for chloride are as follows: zero, 0.03, 0.50, 1.00, 1.50, and 2.00 mg/L as Cl^-.

9.2.2 Prepare all calibration standards by diluting the stock standard (Sect. 7.3) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The standards are stable for one month when stored at room temperature in high density polyethylene or polypropylene containers.

9.3 CALIBRATION CURVE

9.3.1 Analyze the standard containing the highest concentration of chloride and adjust the colorimeter calibration control to obtain full-scale deflection on the recorder. Use the zero standard to set the instrument baseline. If a printer is used, adjust it to read the correct concentration. Analyze all the standards and construct a calibration curve according to Sect. 12. After every 30 samples and at the end of the day's analyses, reconstruct the entire calibration curve.

9.3.2 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.5.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.5). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.4 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 2. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.6), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined

at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the chloride concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample (QCS) after the calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the system or the calibration procedure. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.5). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Optimize the instrument each day according to Sect. 9.1.

11.2 Prepare all standards and construct a calibration curve according to Sect. 9.2 and 9.3.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.4 Load the sampler tray and begin analysis.

11.5 If the peak height response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.6 When analysis is complete, rinse the system with sampler rinse water (Sect. 7.6) for 15 minutes. Rinse with 7.2 N sulfuric acid (Sect. 7.7) for 15 minutes, and repeat the water rinse for 15 minutes.

11.7 Collect chloride waste from the flowcell, place in a fume hood, and add 20 mL of 13% thioacetamide solution per liter of chloride waste. Cap the container and mix well. A precipitate of mercuric sulfide will form. After 24 hours, filter the solution in a fume hood. Discard the filtrate and store the residue of mercuric sulfide in a closed glass container for later disposal at a hazardous waste treatment/storage facility.

12. CALCULATIONS

12.1 Calculate a linear least squares fit of the standard concentrations as a function of the measured peak height. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in mg/L
x = peak height measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of peak heights measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of chloride from the calibration curve.

12.2 If the relationship between standard concentration and measured peak height is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2 x^2 + B_1 x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of chloride from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of chloride.

12.4 Report data in mg/L as Cl. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.6). The results are summarized in Table 1. A small but statistically significant bias of 0.04 mg/L was determined at a spike concentration of 0.41 mg/L. No statistically significant bias was present at a spike concentration of 0.14 mg/L.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 2.

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14.6 Annual Book of ASTM Standards, Section 11, **Vol. 11.01 (1)**, "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Single-Operator Precision and Bias for Chloride Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Chloride	0.14	10	107.1	0.01	0.01	No
	0.41	10	109.5	0.04	0.01	Yes

a. Number of replicates
b. 95% Confidence Level

Table 2. Single-Operator Precision and Bias for Chloride Determined from Quality Control Check Samples.

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias,		Precision,	
			mg/L	%	s, mg/L	RSD, %
0.85	0.88	105	0.03	3.5	0.02	2.3
1.78	1.87	105	0.09	5.1	0.03	1.6

The above data were obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

a. Number of replicates

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Chloride

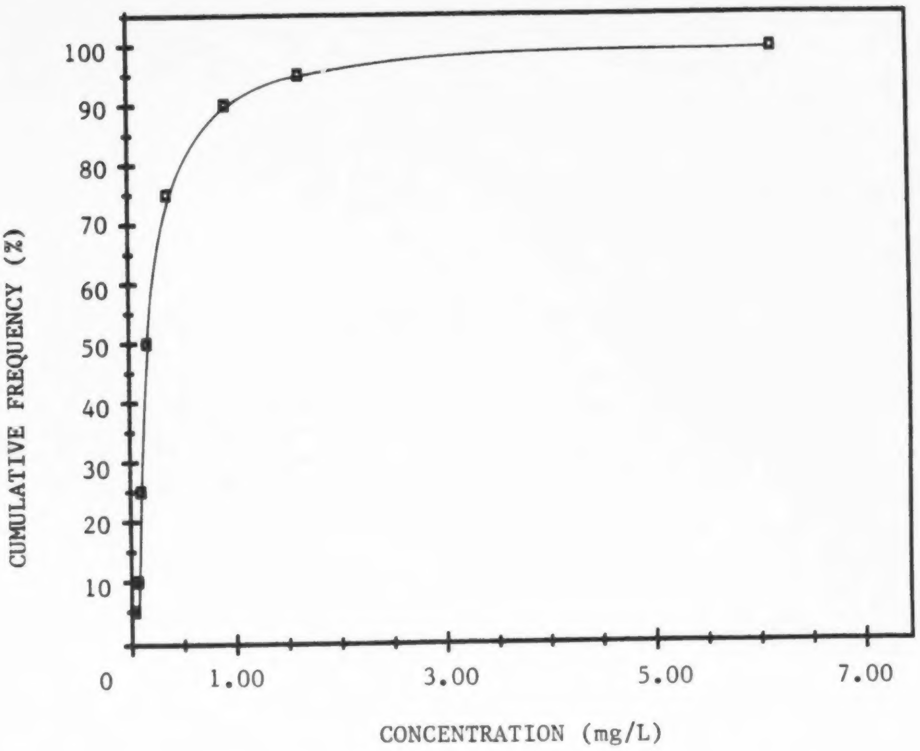
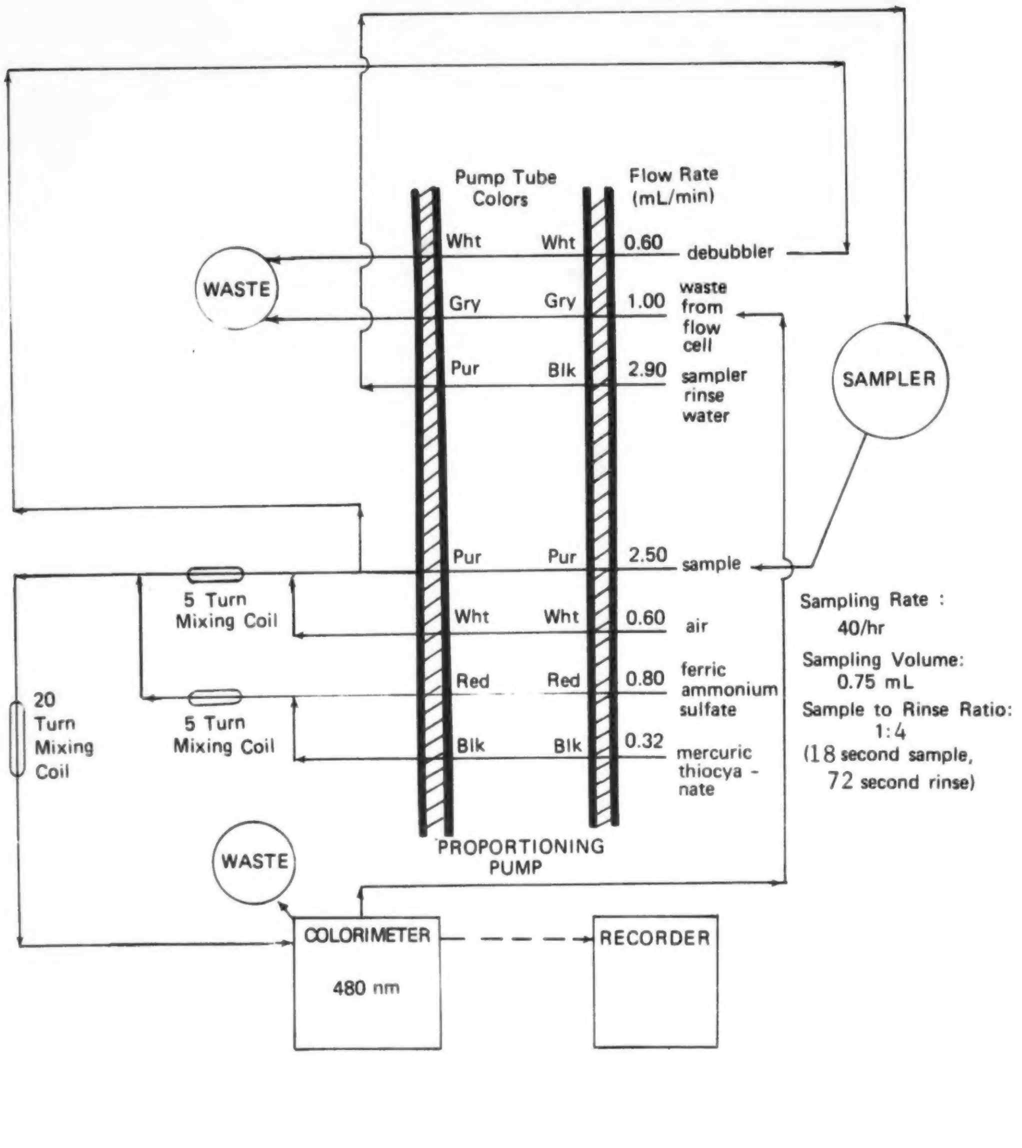


Figure 2. Chloride Sampling and Analytical System -- Segmented Flow.


Pump Tube Colors
Flow Rate (mL/min)
Wht Wht 0.60 debubbler
WASTE
Gry Gry 1.00 waste from flow cell
Pur Blk 2.90 sampler rinse water
SAMPLER
Pur Pur 2.50 sample
Wht Wht 0.60 air
Red Red 0.80 ferric ammonium sulfate
Blk Blk 0.32 mercuric thiocya - nate
5 Turn Mixing Coil
5 Turn Mixing Coil
20 Turn Mixing Coil
Sampling Rate : 40/hr
Sampling Volume: 0.75 mL
Sample to Rinse Ratio: 1:4
(18 second sample, 72 second rinse)
PROPORTIONING PUMP
WASTE
COLORIMETER 480 nm
RECORDER

Method 340.6 -- Fluoride in Wet Deposition by Potentiometric Determination Using an Ion-Selective Electrode

March 1986

Performing Laboratory:

Kenni O. James
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Values for 2.3026 RT/F at Different Temperatures.
2. Single-Operator Precision and Bias for Fluoride Determined from Analyte Spikes of Wet Deposition Samples.
3. Single-Operator Precision and Bias for Fluoride Determined from Quality Control Check Samples.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the potentiometric determination of fluoride in wet deposition samples using an ion-selective electrode as the sensor.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a quality control check solution containing 0.011 mg/L fluoride is 0.003 mg/L. The concentration range over which this method is applicable is 0.003-0.10 mg/L as F^-.

1.4 Fluoride concentrations in wet deposition samples range from 0.003-1.00 mg/L. Average concentrations are in the range of 0.01-0.10 mg/L. Fluoride concentrations as high as 10.00 mg/L have been reported in wet deposition samples collected near industrial sources (14.1).

2. SUMMARY OF METHOD

2.1 Ion-selective electrodes approximate the concentration of specific ions in solution according to the electrode potential that develops across the sensing membrane. In the case of the fluoride electrode, this potential, which depends on the level of free fluoride ion in solution, is measured against a constant reference potential. The measured potential corresponding to the level of fluoride ion in solution is described by the Nernst equation:

$$E = E_o - \frac{2.3026\ RT}{nF} \log [F]$$

where: E = measured electrode potential
E_o = reference potential (a constant)
R = gas constant
T = absolute temperature $[T(^{\circ}C) + 273]$
F = Faraday's constant
n = number of electrons transferred
$[F]$ = molar concentration of fluoride in solution

Values of the factor 2.3026 RT/F at different temperatures are provided in Table 1. The meter and the associated fluoride and reference electrode are calibrated with standard fluoride solutions. A calibration curve is constructed from which the concentration of fluoride in a wet deposition sample is determined.

3. DEFINITIONS

3.1 For definitions of terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 The sample pH must be >5 to avoid complexation by hydrogen ions and <7 to avoid hydroxide interference. The addition of total ionic strength adjustment buffer (TISAB II) to samples will eliminate this potential source of error as well as eliminate possible interferences from aluminum and iron complexation.

5. SAFETY

5.1 The calibration standards, sample types, and most of the reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling sodium hydroxide (Sect. 7.4) and glacial acetic acid (Sect. 7.5).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.3).

6. APPARATUS AND EQUIPMENT

6.1 SPECIFIC ION OR mV METER -- The meter must have a readability of 0.1 mV with an analog or digital display. A meter that has separate calibration and slope adjustment features and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be powered by battery or by 110 VAC. If battery powered, the meter must have a battery check feature. A temperature compensator control to provide accurate measurements at temperatures other than 25°C is desirable.

6.2 SENSING ELECTRODE -- The most commonly used fluoride electrode consists of a single-crystal lanthanum fluoride membrane which is an ionic conductor in which only fluoride ions are mobile. Select an electrode with a concentration range of 0.01 to 1.00 mg/L, a temperature range of 20°-30°C, and a reproducibility of ±2%. Store the electrode according to manufacturer's guidelines.

6.3 REFERENCE ELECTRODE -- Select a single junction Ag/AgCl sleeve type reference electrode for analysis. Store the electrode according to manufacturer's guidelines.

6.4 COMBINATION FLUORIDE ION-SELECTIVE ELECTRODE -- Due to sample volume limitations in wet deposition samples, a combination fluoride electrode that contains both the sensing and the reference elements in one probe is recommended over using two separate electrodes. Use a combination electrode with a single junction Ag/AgCl sleeve type reference element (Orion #96-09 or equivalent). When not in use, store the combination fluoride electrode according to manufacturer's guidelines.

6.5 STIRRING DEVICE (electric or water-driven) -- If an electric stirrer is selected, place an air gap or insulating pad between the stirrer surface and the solution container to minimize heating of the sample. Use a Teflon-coated stirring bar.

6.6 THERMOMETER -- Select a thermometer capable of being read to the nearest 1°C and covering the range 0°-40°C.

6.7 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.4). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 FLUORIDE SOLUTION, STOCK (1.0 mL = 1.0 mg F) -- The stock solution may be purchased as a certified solution or prepared from ACS reagent grade materials. To prepare, dissolve 0.221 g of anhydrous sodium fluoride (NaF) in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container.

7.4 SODIUM HYDROXIDE SOLUTION (5.0 N) -- Dissolve 200.0 g of sodium hydroxide (NaOH) slowly in 500 mL of water (Sect. 7.2). Cool to room temperature and dilute to 1 L with water (Sect. 7.2).

7.5 TOTAL IONIC STRENGTH ADJUSTMENT BUFFER (TISAB II for low level measurements) -- Add 57.0 mL of glacial acetic acid (CH_3COOH), 4.0 g of cyclohexylene dinitrilo tetraacetic acid (CDTA), and 58.0 g of sodium chloride (NaCl) to 500 mL of water (Sect. 7.2). Stir to dissolve and cool to room temperature. Add 150 mL of 5 N NaOH. Cool to room temperature and dilute to 1 L with water (Sect. 7.2). Store at room temperature in a polyolefin container. Add to standards and samples as directed in Sect. 9.5.2 and Sect. 11.4 to provide a constant background ionic strength and to maintain the pH of the solution between 5.0 and 5.5.

7.5 SAMPLE CONTAINERS -- Use polyolefin sample cups that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods.

8.3 Fluoride concentrations are stable in natural waters for 28 days when stored at 25°C in high density polyethylene or polypropylene containers (14.5). No data are available for the stability of fluoride in wet deposition samples.

9. CALIBRATION AND STANDARDIZATION

9.1 Turn on the meter and allow it to warm up according to manufacturer's instructions. If an ion selective meter is used, set the function switch to detect monovalent anions.

9.2 If necessary, add filling solution supplied by the manufacturer to the electrode before using. Maintain the filling solution level at least one inch above the level of the sample surface to ensure proper electrolyte flow rate.

9.3 Bring all standards and samples to ambient temperature before beginning any analyses. Maintain samples and standard solutions within ±1°C of each other and maintain operating temperatures of 25 ± 2°C (14.6). The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibrium upon which the electrode depends. The slope of the fluoride electrode also varies with temperature as indicated in the Nernst equation in Sect. 2.1.

9.4 CALIBRATION SOLUTIONS

9.4.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain fluoride at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of fluoride in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for fluoride are as follows: zero, 0.01, 0.03, 0.05, 0.07, and 0.10 mg/L as F^-.

9.4.2 Prepare all calibration standards by diluting the stock standard (Sect. 7.3) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The standards are stable for one month when stored at room temperature in high density polyethylene or polypropylene containers.

9.5 ELECTRODE SLOPE -- Check the electrode slope daily before any analyses are performed. Use two fluoride solutions that differ from one another in concentration by a factor of ten and are within the working concentration range. Suitable solutions to be used for this procedure are the 0.01 and 0.10 mg/L calibration standards prepared in Sect. 9.4.1.

9.5.1 Rinse the sample cup with three changes of water (Sect. 7.2). Pipette a minimum of 5 mL of 0.01 mg/L calibration standard into the sample cup. Add TISAB II in a 1:1 volumetric ratio and equilibrate for at least 15 minutes for complete Al^{+3} and Fe^{+3} complexation. Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Blot the electrode(s) dry with a clean laboratory tissue and immerse into the 0.01 mg/L standard to which TISAB II has been added. Stir the solution and maintain a stirring rate of approximately 4 revolutions per second (rps) throughout the analysis. Allow the electrode about three minutes to stabilize. Adjust the calibration control until the display reads "1" if a specific ion meter is used or until the display reads 0.0 if a mV meter is used.

9.5.2 Dispense an aliquot of 0.10 mg/L calibration standard into a second clean sample cup, add TISAB II, and allow to equilibrate as directed in Sect. 9.5.1. Rinse the electrode(s), blot dry, immerse in the solution, and stir as directed in Sect 9.5.1. Allow the electrode about three minutes to stabilize. If a mV meter is used, correct electrode performance is indicated by a reading of -57±3 mV. If a specific ion meter is used, use the slope adjustment feature to set the display to read "10".

9.5.3 If the slope is not within the acceptable range indicated in Sect. 9.5.2, refer to the electrode instruction manual for corrective action.

9.6 CALIBRATION CURVE

9.6.1 Rinse the sample cup with three changes of water (Sect. 7.2). Pipette an aliquot of zero standard into the sample cup. Add TISAB II in a 1:1 volumetric ratio and equilibrate for at least 15 minutes for complete Al^{+3} and Fe^{+3} complexation. Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Blot the electrode(s) dry with a clean laboratory tissue and immerse into the zero standard to which TISAB II has been added. Stir the solution and maintain a stirring rate of approximately 4 rps throughout the analysis. Allow sufficient time for the reading to remain steady within ±0.01 mg/L or 0.1 mV (depending on the type of meter used) for 30 seconds. When the meter reading is stable, record the measurement.

9.6.2 Analyze the remaining standards in order of increasing fluoride concentration, measuring the most concentrated standard last. Rinse the electrode(s) between standards. Construct a calibration curve according to Sect. 12.

9.6.3 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.6.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.7). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\overline{x}$) for determining the control limits. A warning limit of $\overline{x} \pm 2s$ and a control limit of $\overline{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.5 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 3. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.8), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined

at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water (Sect. 7.2) to remain in the sealed or capped collection container for at least 24 hours and determine the fluoride concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Electrodes used for the measurement of wet deposition samples should not be used for other sample types. Solutions with high concentrations of fluoride may cause electrode degradation and result in biased measurements and/or slow response in wet deposition samples. If the sensing element of the electrode becomes coated with organic deposits, longer response times in dilute fluoride solutions will result. Refer to the manufacturer's guidelines for instructions on how to clean the electrode of organic deposits.

10.5 Analyze a quality control check sample (QCS) after the meter and electrode assembly have been calibrated. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards and should approximate the range of the samples to be analyzed. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the calibration procedure or the electrode/meter assembly. Check the meter according to the manufacturer's guidelines. If an electrode problem is indicated, replace the electrode. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.6 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.5, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.5 and reanalyze all samples analyzed since the last time the system was in control.

10.7 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.8 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.7). Compare the results obtained from the spiked sample to that obtained from an identical sample to which no spike was added. Use these data to determine percent recovery as described in Sect. 10.2.3.

10.9 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Prepare all standards and bring solutions and samples to ambient temperature (±1°C).

11.2 Check electrode slope each day according to Sect. 9.5 and construct a calibration curve according to Sect. 9.6.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.5.

11.4 SAMPLE ANALYSIS

11.4.1 Rinse the sample cup with three changes of water (Sect. 7.2). Dispense an aliquot of sample equivalent to that used for the calibration standards. Add TISAB II in a 1:1 volumetric ratio and allow the solution to equilibrate for at least 15 minutes.

11.4.2 Rinse the electrode(s) with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Blot dry with a clean, absorbent laboratory tissue. Immerse the clean electrode(s) into the sample and observe the meter reading while mixing. When the reading is steady within ±0.01 mg/L or 0.1 mV (depending on the type of meter used) for 30 seconds, record the measurement.

11.5 TISAB to sample volume ratios of 1:10 have been used successfully for the determination of fluoride in wet deposition samples (14.9). The smaller volume of TISAB used in this procedure provides increased method sensitivity for low level analyses.

11.6 Response times for the electrode assembly may be shortened by preconditioning the electrode(s) (14.10). Immerse the clean electrode(s) into a portion of the wet deposition sample to be analyzed, allow the system to equilibrate for approximately three minutes, and remove the electrode. Insert the electrode(s) directly into a second portion of sample and record the reading when the system is stabilized according to Sect. 11.4.2. This procedure, however, is limited by the amount of wet deposition sample available.

11.7 If the concentration of fluoride in a sample exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

12. CALCULATIONS

12.1 Calculate a linear least squares fit of the standard concentration as a function of the measured concentration. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1 x$$

where: y = standard concentration in mg/L
x = concentration measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of concentration measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of fluoride from the calibration curve.

12.2 If the relationship between standard and measured concentration is nonlinear, a second degree polynomial least squares equation can be used to derive an acceptable curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of fluoride from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of fluoride.

12.4 Report data in mg/L as F^-. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.8). The results are summarized in Table 2. A small but statistically significant bias of -0.004 was determined at a spike concentration of 0.027 mg/L. No statistically significant bias was present at a spike concentration of 0.082 mg/L.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 3.

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Table 1. Values for 2.3026 RT/F at Different Temperatures

Temperature, °C	2.3026 RT/F, V
0	0.054
5	0.055
10	0.056
15	0.057
20	0.058
25	0.059
30	0.060
35	0.061
40	0.062
45	0.063

The above data were calculated using a precise value of the logarithmic conversion factor (2.302585) and values of the fundamental constants.

F = 96,487.0 C/eq
R = 8.31433 J/K mol
T = 273.15 + °C

Table 2. Single-Operator Precision and Bias for Fluoride Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Fluoride	0.027	10	87.1	-0.004	0.003	Yes
	0.082	10	98.3	-0.001	0.003	No

a. Number of replicates
b. 95% Confidence Level

Table 3. Single-Operator Precision and Bias for Fluoride Determined from Quality Control Check Samples.[a]

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[b]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
0.0112	0.0108	6	-0.0004	-3.6	0.0010	9.2
0.0560	0.0558	7	-0.0001	-0.2	0.0010	1.8

a. Concentration values are significant to three decimal places.
b. Number of replicates

Method 350.6 -- Ammonium in Wet Deposition by Electrometric Determination Using an Ion-Selective Electrode

March 1986

Performing Laboratory:

Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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1. SCOPE AND APPLICATION

1.1 This method is applicable to the measurement of ammonium in wet deposition samples using an ion-selective electrode as the sensor.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a quality control check solution containing 0.17 mg/L ammonium is 0.05 mg/L. The analyte concentration range over which this method is applicable is 0.05-2.00 mg/L as NH_4^+.

1.4 Figure 1 represents a cumulative frequency percentile ammonium concentration plot obtained from analyses of over five thousand wet deposition samples. These values may be used as an aid in the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 The pH of a solution is adjusted to between 11 and 14 to convert ammonium ion to ammonia gas. A gas sensing ion-selective electrode approximates the concentration of ammonia in solution according to the electrode potential that develops across the sensing membrane. This potential is measured against a constant reference potential according to the Nernst equation:

$$E = E_o - \frac{2.3026\ RT}{nF} \log [NH_3]$$

where: E = measured electrode potential
E_o = reference potential (a constant)
R = gas constant
T = absolute temperature $[T(^{o}C) + 273]$
F = Faraday's constant
n = number of electrons transferred
$[NH_3]$ = molar concentration of ammonia in solution

Values of the factor 2.3026 RT/F at different temperatures are provided in Table 1. The meter and the ammonia electrode are calibrated with standard ammonium solutions. A calibration curve is constructed from which the concentration of ammonium ion in a wet deposition sample is determined.

3. DEFINITIONS

3.1 For definitions of terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.1).

4. INTERFERENCES

4.1 Stirring rates that form a vortex will result in ammonia loss. A stirring rate of approximately two revolutions per second is recommended. Maintain a constant stirring rate throughout analyses of all standards and samples.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling sodium hydroxide (Sect. 7.4).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.2).

6. APPARATUS AND EQUIPMENT

6.1 SPECIFIC ION OR mV METER -- The meter must have a readability of 0.1 mV with an analog or digital display. A meter that has separate calibration and slope adjustment features and is electrically shielded to avoid interferences from stray currents or static charge is necessary. It may be powered by battery or by 110 VAC; if battery powered, the meter must have a battery check feature.

6.2 AMMONIA ION-SELECTIVE ELECTRODE -- Select a gas-sensing ammonia electrode containing a reference element with a liquid internal filling solution in contact with a hydrophobic gas-permeable membrane. Select an electrode that has a concentration range of 0.05 to 2.00 mg/L ammonium and a temperature range of 20°-30°C with a reproducibility of ±2%. When not in use, store the electrode according to manufacturer's guidelines.

6.3 STIRRING DEVICE (electric or water-driven) -- If an electric stirrer is selected, leave an air gap or place an insulating pad between the stirrer surface and the solution container to prevent heating of the sample. Use a tetrafluoroethylene (TFE)-coated stirring bar.

6.4 THERMOMETER -- Select a thermometer capable of being read to the nearest 1°C and covering the range 0°-40°C.

6.5 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.3). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 AMMONIUM SOLUTION, STOCK (1.0 mL = 1.0 mg NH_4) -- The stock solution may be purchased as a certified solution or prepared from ACS reagent grade materials. To prepare, dissolve 2.9654 g of ammonium chloride (NH_4Cl), dried at 105°C for 1 hour, in water (Sect. 7.2) and dilute to 1 L. The stock solution is stable for one year when refrigerated at 4°C in a high density polyethylene or polypropylene container.

7.4 SODIUM HYDROXIDE SOLUTION (2.0 N) -- Prepare a dilute sodium hydroxide (NaOH) solution by dissolving 80.0 g of reagent grade sodium hydroxide (NaOH) in water (Sect. 7.2) and diluting to 1 L. Store at room temperature in a high density polyethylene or polypropylene container for a period not exceeding one year.

7.5 SAMPLE CONTAINERS -- Use glass or polyolefin sample cups that have been rinsed thoroughly with water (Sect. 7.2) before use. To reduce the opportunity for ammonia loss to the ambient atmosphere, select sample containers designed to minimize the ratio of surface area to sample volume.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The presence of microbial activity will affect the stability of ammonium concentrations in wet deposition samples. Chemical determinations should be made immediately after collection whenever possible.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is partially effective at stabilizing ammonium by removal of biologically active species. Refrigeration after immediate filtration is the most reliable method to ensure sample integrity (14.4). Sample storage time should not exceed one week.

9. CALIBRATION AND STANDARDIZATION

9.1 Turn on the meter and allow it to warm up thoroughly according to the manufacturer's instructions. If an ion selective meter is used, set the function switch to detect monovalent anions.

9.2 If necessary, add filling solution to the electrode before using. To improve electrode response at low concentrations, prepare a 1:10 dilution of the internal filling solution by adding 1 mL of solution to 10 mL of water (Sect. 7.2) (14.5). Maintain the filling solution level at least one inch above the level of the sample surface to ensure proper electrolyte flow rate.

9.3 Bring all standards and samples to ambient temperature before beginning any analyses. Maintain samples and standard solutions within ±1°C of each other and maintain operating temperatures of 25 ± 2°C during analyses to minimize ammonia loss from solutions. The absolute potential of the reference element changes slowly with temperature because of the solubility equilibrium upon which the electrode depends. The slope of the ammonia electrode also varies with temperature as indicated in the Nernst equation in Sect. 2.1.

9.4 CALIBRATION SOLUTIONS

9.4.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain ammonium at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of ammonium in wet deposition. Prepare the remaining solutions such that they evenly encompass the concentration range. Suggested calibration standards for ammonium are as follows: zero, 0.05, 0.50, 1.00, 1.50, and 2.00 mg/L as NH_4^+.

9.4.2 Prepare all calibration standards by diluting the stock standard (Sect. 7.3) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The standards are stable for one week when refrigerated at 4°C in high density polyethylene or polypropylene containers.

9.5 ELECTRODE SLOPE -- Check the electrode slope daily before any analyses are performed. Use two ammonium solutions that differ from one another in concentration by a factor of ten and are within the range of subsequent ammonium analyses. Suitable solutions to be used for this procedure are the 0.20 and 2.00 mg/L calibration standards prepared in Sect. 9.4.1.

9.5.1 Rinse the electrode and the sample cup with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Immerse the electrode into the 0.20 mg/L calibration standard. Add 1 mL of NaOH solution to 15 mL of standard solution. Stir the solution while maintaining a stirring rate of approximately 2 rps throughout the analysis. Allow the electrode to stabilize for two minutes. Adjust the calibration control until the display reads "1" if a specific ion meter is used or until the display reads 000.0 if a mV meter is used.

9.5.2 Rinse the electrode, add an equal volume aliquot of 2.00 mg/L standard to the sample cup, add 1 mL of NaOH, and stir as directed in Sect. 9.5.1. Allow the electrode to equilibrate for two minutes. If a mV meter is used, correct electrode operation is indicated by a reading of -57 ± 3 mV. If a specific ion meter is used, use the slope adjustment feature to set the display to read "10".

9.5.3 If the slope is not within the acceptable range indicated in Sect. 9.5.2, refer to the electrode instruction manual for corrective action.

9.6 CALIBRATION CURVE

9.6.1 Rinse the electrode and the sample cup with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle. Immerse the electrode into the zero standard. Add the NaOH solution (1 mL of NaOH:15 mL standard) to adjust the pH of the solution to between 11 and 14. Stir the solution and maintain a stirring rate of approximately 2 rps throughout the analysis. Allow sufficient time for the reading to remain steady within ±0.01 mg/L or 0.1 mV (depending on the meter used) for 30 seconds. When the meter reading is stable, record the measurement.

9.6.2 Rinse the electrode. Analyze the remaining standards in order of increasing ammonium concentration, measuring the most concentrated standard last. Rinse the electrode between standards. Construct a calibration curve according to Sect. 12.

9.6.3 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.6.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.6). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.5 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 3. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.7), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined

at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of deionized water that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the ammonium concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Electrodes used for the measurement of wet deposition samples should not be used for other sample types.

10.5 Analyze a quality control check sample (QCS) after the meter and electrode assembly have been calibrated. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards and should approximate the range of the samples to be analyzed. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the calibration procedure or the electrode/meter assembly. Check the meter according to the manufacturer's guidelines. If an electrode problem is indicated, replace the electrode. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.6 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.5, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.5 and reanalyze all samples analyzed since the last time the system was in control.

10.7 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.8 Prepare and analyze a laboratory spike of a wet deposition sample standard according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.6). Compare the results obtained from the spiked sample to that obtained from an identical sample to which no spike was added. Use these data to determine percent recovery as described in Sect. 10.2.3.

10.9 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Prepare all standards and bring solutions and samples to ambient temperature ($\pm 1^{\circ}$C).

11.2 Check electrode slope each day according to Sect. 9.5 and construct a calibration curve according to Sect. 9.6.

11.3 To minimize the loss of ammonia from the sample to the ambient atmosphere, do not dispense the samples or standards until immediately before measurement. Do not adjust the pH of the solutions until the electrode is immersed in the sample.

11.4 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.5.

11.5 SAMPLE ANALYSIS

11.5.1 Rinse the electrode and the sample cup with three changes of water (Sect. 7.2) or with a flowing stream from a wash bottle.

11.5.2 Measure an aliquot of sample equivalent to that used for the calibration standards. Immerse the clean electrode into the sample and add NaOH (1 mL NaOH:15 mL sample). Stir the solution while maintaining a stirring rate of approximately 2 rps throughout the analysis. Allow sufficient time for the reading to remain steady within ±0.01 mg/L or 0.1 mV (depending on the meter used) for 30 seconds. When the meter reading is stable, record the measurement.

11.6 If the concentration of ammonium in a sample exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

12. CALCULATIONS

12.1 Calculate a linear least squares fit of the standard concentration as a function of the measured concentration. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1x$$

where: y = standard concentration in mg/L
x = concentration measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of concentrations measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of ammonium from the calibration curve.

12.2 An integration system may also be used to provide a direct readout of the concentration of ammonium.

12.3 Report data in mg/L as NH_4^+. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.7). The results are summarized in Table 2. A small but statistically significant bias of 0.05 mg/L was determined at a spike concentration of 0.25 mg/L. No statistically significant bias was present at a spike concentration of 0.10 mg/L.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 3.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.2 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.3 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.4 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. **12**, 1978, pp. 2343-2349.

14.5 Orion Research, Inc., "Instruction Manual -- Ammonia Electrode, Model 95-12," Orion Research, Inc., Cambridge, Massachusetts, 1982, pp. 1-17.

14.6 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.7 Annual Book of ASTM Standards, Section 11, **Vol. 11.01 (1)**, "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Values for 2.3026 RT/F at Different Temperatures.

Temperature, °C	2.3026 RT/F, V
0	0.054
5	0.055
10	0.056
15	0.057
20	0.058
25	0.059
30	0.060
35	0.061
40	0.062
45	0.063

The above data were calculated using a precise value of the logarithmic conversion factor (2.302585) and values of the fundamental constants.

F = 96,487.0 C/eq
R = 8.31433 J/K mol
T = 273.15 + °C

Table 2. Single-Operator Precision and Bias for Ammonium Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Ammonium	0.10	10	125.0	0.02	0.02	No
	0.25	8	119.0	0.05	0.01	Yes

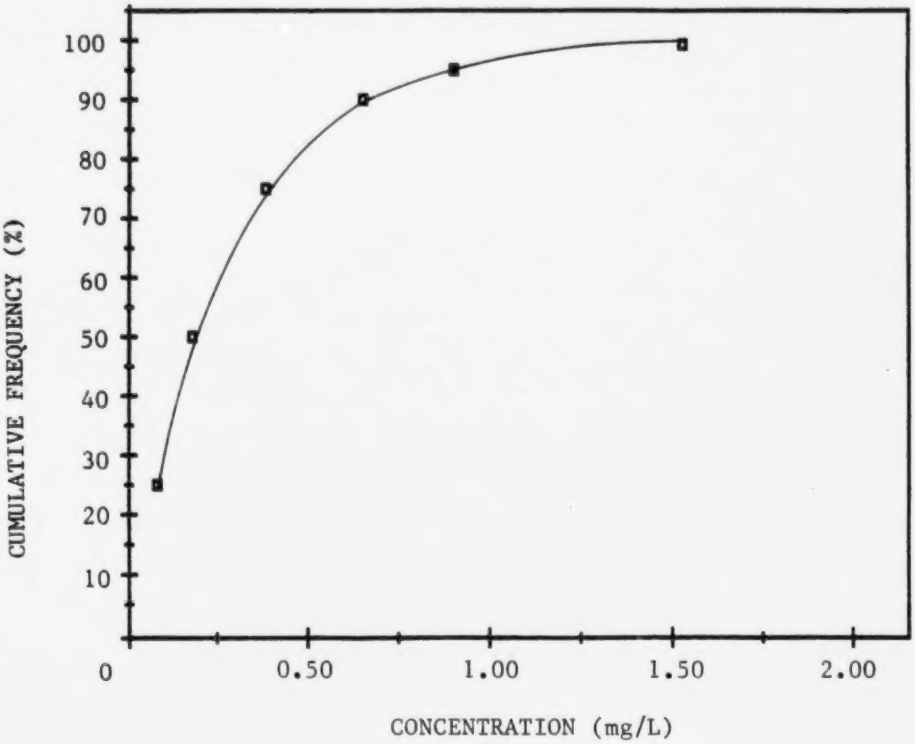
a. Number of replicates
b. 95% Confidence Level

Table 3. Single-Operator Bias and Precision for Ammonium Determined from Quality Control Check Samples.

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
0.18	0.17	12	-0.01	-5.6	0.018	10.6
0.39	0.38	12	-0.01	-2.6	0.025	6.6

a. Number of replicates

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Ammonium



Method 350.7 -- Ammonium in Wet Deposition by Automated Colorimetric Determination with Phenate

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Performing Laboratory:

Brigita Demir
Susan R. Bachman
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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1. Single-Operator Precision and Bias for Ammonium Determined from Analyte Spikes of Wet Deposition Samples.
2. Single-Operator Precision and Bias for Ammonium Determined from Quality Control Check Samples.

FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples: Ammonium.
2. Ammonium Sampling and Analytical System -- Segmented Flow.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the automated colorimetric determination of ammonium in wet deposition samples by reaction with phenate.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a calibration standard containing 0.10 mg/L ammonium is 0.03 mg/L. The concentration range of this method is 0.03-2.00 mg/L as NH_4^+.

1.4 Figure 1 represents a cumulative frequency percentile ammonium concentration plot obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 A sample is introduced into the automated analyzer and mixed with a complexing reagent to prevent the formation of hydroxide precipitates. This solution is then mixed with alkaline phenol and hypochlorite to form an indophenol blue complex. The blue color is intensified with the addition of sodium nitroprusside. A 50°C controlled temperature heating bath is used to increase the rate of color formation. After color development, a flowcell receives the solution for measurement of the color intensity. A light beam of the wavelength characteristic of the indophenol complex is passed through the solution. The transmitted light energy measured by a photodetector is a function of the concentration of ammonium ion in the sample. Beer's Law is used to relate the measured transmittance to concentration:

$$\log(1/T) = abc$$

where: T = transmittance
a = absorptivity
b = length of light path
c = concentration of absorbing species (mg/L)

A calibration curve is constructed using standard solutions containing known concentrations of ammonium. From this curve, the concentration of ammonium in a wet deposition sample is determined.

3. DEFINITIONS

3.1 COLORIMETRY -- the measurement of light transmitted by a colored complex as a function of concentration.

3.2 For definitions of other terms used in these methods, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.1).

4. INTERFERENCES

4.1 Sample color absorbing in the wavelength range of 620-640 nm will increase the measured concentration of ammonium in the sample. Wet deposition samples are generally colorless, therefore, this type of interference is rare.

4.2 Elevated concentrations of ammonia in the laboratory will result in a positive interference.

5. SAFETY

5.1 The calibration standards, sample types and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated sulfuric acid (Sect. 7.5).

5.2 Use a fume hood when preparing the alkaline phenol (Sect. 7.3). Vapors produced by this reagent are hazardous. Anytime this solution is handled, wear gloves and safety goggles and avoid all skin contact with the phenol.

5.3 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.2).

6. APPARATUS AND EQUIPMENT

6.1 AUTOMATED COLORIMETRIC INSTRUMENT -- Select and assemble an analytical system consisting of the following:

6.1.1 Sampler.

6.1.2 Proportioning Pump.

6.1.3 Analytical Cartridge.

6.1.4 Heating Bath (50°C) equipped with an 8 mL capacity glass heating coil.

6.1.5 Colorimeter with a 630 nm wavelength setting. Ensure that the colorimeter is equipped with photodetectors having maximum sensitivity at this wavelength setting. A 15 mm flow cell is adequate to achieve the MDL stated in Sect. 1.3.

6.1.6 Strip Chart Recorder (or other data acquisition device).

6.1.7 Printer (optional).

6.2 Wherever possible, use glass transmission lines with an inside diameter of 1.85 mm (0.073 inches) in the analytical cartridge and colorimeter. Glass yields a more uniform sample flow and does not degrade as quickly as other tubing materials. When connecting two glass lines, ensure that the ends are abutted. To minimize pulsing of the analytical stream, maintain uniform inside diameter throughout all transmission tubing. Minimize the length of all transmission tubing to optimize the performance of the hydraulic system.

6.3 Enclose the sampler with a dust cover to prevent contamination.

6.4 To prevent the intake of any precipitates from the reagents, install intake filters at the end of the transmission lines that are used to transport the reagents from their respective containers to the proportioning pump.

6.5 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.3). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 ALKALINE PHENOL -- Add 35 g of sodium hydroxide (NaOH) to 250 mL of water (Sect. 7.2). Stir and cool. Slowly add 85 mL of 88% (w/w) phenol solution. Dilute to 500 mL with water (Sect. 7.2) and add 0.25 mL Brij-35 or another suitable wetting agent that is free from ammonium. Refrigerate the solution at 4°C in an amber glass container for a period not exceeding one week.

CAUTION: The vapors produced by the alkaline phenol solution are hazardous. Avoid all respiratory and skin contact with this reagent. Refer to Sect. 5.2 for an explanation of necessary safety precautions.

7.4 AMMONIUM SOLUTION, STOCK (1.0 mL = 1.0 mg NH_4) -- Dissolve 2.9654 g of anhydrous ammonium chloride (NH_4Cl), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L. The stock solution is stable for one year when stored at room temperature in a high density polyethylene or polypropylene container.

7.5 COMPLEXING REAGENT -- Dissolve 33 g of potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$) and 24 g of sodium citrate ($(HOC(COONa)CH_2COONa)_2 \cdot 2H_2O$) in 950 mL of water (Sect. 7.2). Add 2.5 mL of concentrated sulfuric acid (H_2SO_4, sp gr 1.84). Dilute to 1 L with water (Sect. 7.2) and refrigerate at 4°C in a glass container.

7.6 SAMPLER RINSE WATER -- Add 0.5 mL Brij-35 or another suitable wetting agent that is free from ammonium to 1 L of water (Sect. 7.2).

7.7 SODIUM HYPOCHLORITE SOLUTION (1.75% w/v) -- Dilute 100 mL of 5.25% (w/v) sodium hypochlorite (NaOCl) solution to 300 mL with water (Sect. 7.2). Prepare this solution fresh daily and store at room temperature in a high density polyethylene or polypropylene container. Commercial bleach products containing about 5.25% (w/v) sodium hypochlorite may be used. Due to the instability of commercial bleaches, avoid storage periods longer than six months.

7.8 SODIUM NITROPRUSSIDE SOLUTION (500 mg/L) -- Dissolve 0.5 g of sodium nitroprusside ($Na_2Fe(CN)_5NO \cdot H_2O$) in water (Sect. 7.2) and dilute to 1 L. Store at room temperature away from light in an amber glass container.

7.9 SAMPLE CONTAINERS -- Use polyolefin sample cups or glass test tubes that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The presence of microbial activity will affect the stability of ammonium ion in wet deposition samples. This instability generally results in a decrease in ammonium concentration. Measurements of NH_4^+ should be made immediately after sample collection. Refrigeration of samples at 4°C will minimize but not prevent a decrease in the ammonium ion concentration.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) followed by refrigeration at 4°C is the recommended preservation technique for ammonium ion. Holding times should not exceed seven days. Monitoring of the filtration procedure is necessary to ensure that samples are not contaminated by the membrane or filtration apparatus.

9. CALIBRATION AND STANDARDIZATION

9.1 INSTRUMENT OPTIMIZATION

9.1.1 For a flow segmented system with a concentration range from 0.03-2.00 mg/L as ammonium, assemble the sampling and analytical system as shown in Figure 2.

9.1.2 Use flow rated polyvinyl chloride (PVC) or polyethylene pump and transmission tubing throughout the sampling and analytical system. Check the tubing for chemical buildup, splits, cracks, and deformations before beginning each day's analysis. Change pump tubes after 50 hours of operation. Change transmission tubing after 100 hours of operation or when uneven flow patterns are observed.

9.1.3 Optimize the tension of the pump tubes according to manufacturer's recommendations.

9.1.4 Set the heating bath to 50°C. Set the wavelength of the colorimeter to 630 nm. Allow the colorimeter and heating bath to warm up for 30 minutes while pumping sampler rinse water and reagents through the system. After a stable baseline has been obtained, adjust the recorder to maximize the full-scale response.

9.1.5 Sample at a rate of 40 samples/hour with a 1:4 sample to rinse ratio. This sampling rate provides good peak separation. Adjust the colorimeter to maximize sensitivity while minimizing instrument noise. Refer to the manufacturer's recommendations.

9.2 CALIBRATION SOLUTIONS

9.2.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain ammonium at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of ammonium in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for ammonium are as follows: zero, 0.03, 0.40, 0.75, 1.00, and 1.50 mg/L as NH_4^+.

9.2.2 Prepare all calibration standards by diluting the stock standard (Sect. 7.4) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. Standards with a concentration greater than 0.10 mg/L ammonium are stable for one week if stored at room temperature in high density polyethylene or polypropylene containers. Prepare standards with 0.10 mg/L or less ammonium every day and store at room temperature in high density polyethylene or polypropylene containers.

9.3 CALIBRATION CURVE

9.3.1 Analyze the standard containing the highest concentration of ammonium and adjust the colorimeter calibration control to obtain full-scale deflection on the recorder. Use the zero standard to set the instrument baseline. If a printer is used, adjust it to read the correct concentration. Analyze all the standards and construct a calibration curve according to Sect. 12. After every 30 samples and at the end of each day's analyses, reconstruct the entire calibration curve.

9.3.2 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.5.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.4). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\overline{x}$) for determining the control limits. A warning limit of $\overline{x} \pm 2s$ and a control limit of $\overline{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.4 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 2. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using ±2s and ±3s, respectively. If the data indicate that no significant method bias exists (14.5), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the ammonium concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample (QCS) after the calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the system or the calibration procedure. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.4). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Optimize the instrument each day according to Sect. 9.1.

11.2 Prepare all standards and construct a calibration curve according to Sect. 9.2 and 9.3.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.4 Load the sampler tray and begin analysis.

11.5 If the peak height response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.6 When analysis is complete, turn off the heating bath and rinse the system with sampler rinse water (Sect. 7.6) for 15 minutes.

12. CALCULATIONS

12.1 Calculate a linear least squares fit of the standard concentration as a function of the measured peak height. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1x$$

where: y = standard concentration in mg/L
x = peak height measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n} (x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of peak heights measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of ammonium from the calibration curve.

12.2 If the relationship between standard concentration and measured peak height is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of ammonium from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of ammonium.

12.4 Report data in mg/L as NH_4^+. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.5). The results are summarized in Table 1. No statistically significant biases were found.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 2.

14. REFERENCES

14.1 *Annual Book of ASTM Standards*, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.2 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.3 *Annual Book of ASTM Standards*, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.4 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., *Quality Assurance Manual for Precipitation Measurement Systems*, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.5 *Annual Book of ASTM Standards*, Section 11, **Vol. 11.01 (1)**, "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Single-Operator Precision and Bias for Ammonium Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Ammonium	0.17	8	100.0	-0.01	0.01	No
	0.74	10	103.4	0.02	0.03	No

a. Number of replicates
b. 95% Confidence Level

Table 2. Single-Operator Bias and Precision for Ammonium Determined from Quality Control Check Samples.

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
0.19	0.18	215	-0.01	-5.3	0.02	11.1
0.36	0.36	82	0.00	0.0	0.02	5.6
0.98	0.92	224	-0.06	-6.1	0.05	5.4
1.22	1.24	81	0.02	1.6	0.03	2.4

The above data were obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

[a] Number of replicates

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Ammonium

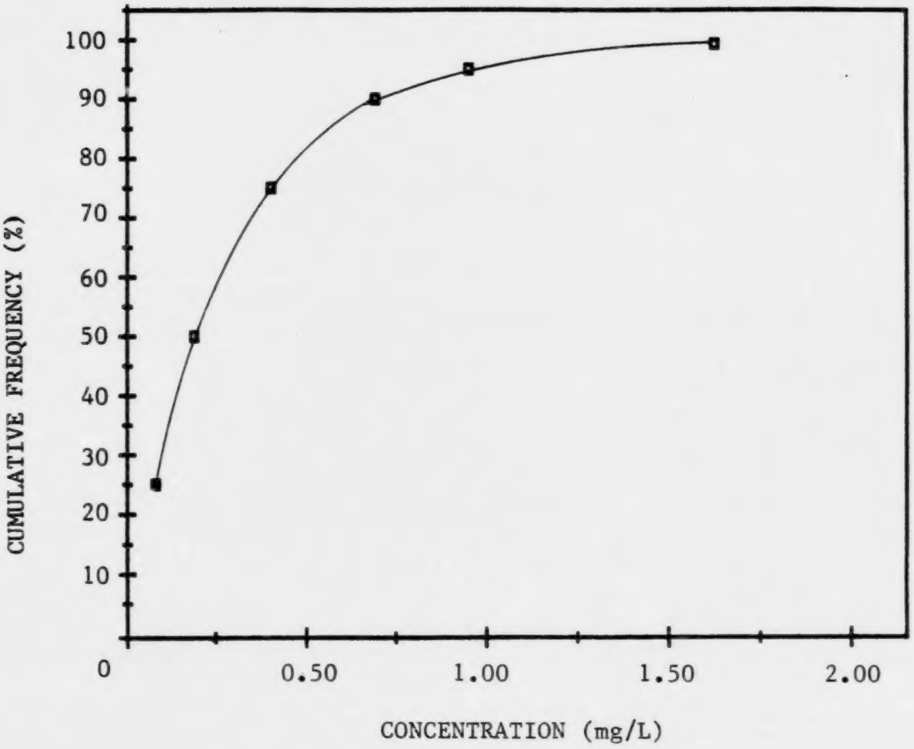
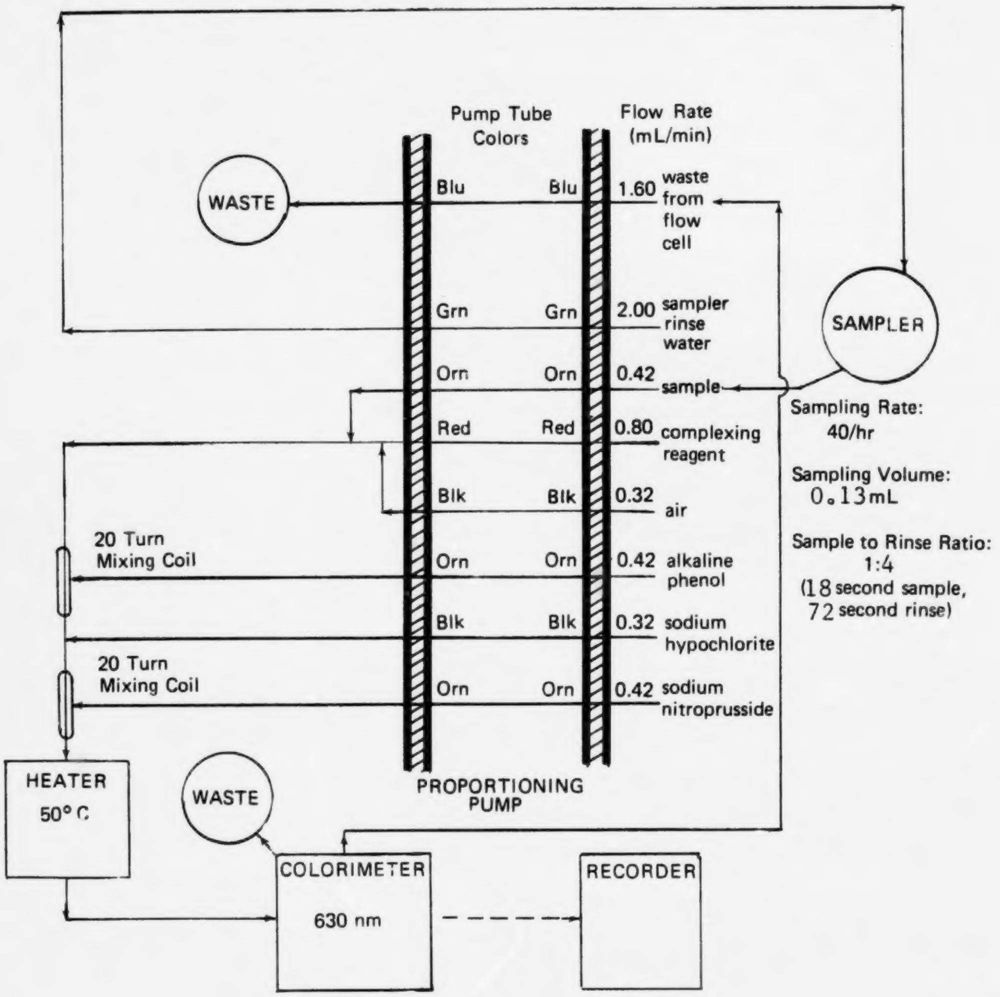


Figure 2. Ammonium Sampling and Analytical System -- Segmented Flow.


Pump Tube Colors
Flow Rate (mL/min)
WASTE
Blu
Blu
1.60 waste from flow cell
Grn
Grn
2.00 sampler rinse water
SAMPLER
Orn
Orn
0.42 sample
Red
Red
0.80 complexing reagent
Blk
Blk
0.32 air
Sampling Rate: 40/hr
Sampling Volume: 0.13mL
Sample to Rinse Ratio: 1:4 (18 second sample, 72 second rinse)
20 Turn Mixing Coil
Orn
Orn
0.42 alkaline phenol
Blk
Blk
0.32 sodium hypochlorite
20 Turn Mixing Coil
Orn
Orn
0.42 sodium nitroprusside
HEATER 50° C
WASTE
PROPORTIONING PUMP
COLORIMETER 630 nm
RECORDER

Method 353.6 -- Nitrate-Nitrite in Wet Deposition by Automated Colorimetric Determination using Cadmium Reduction

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Performing Laboratory:

Brigita Demir
Susan R. Bachman
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Single-Operator Bias and Precision for Nitrate-Nitrite Determined from Analyte Spikes of Wet Deposition Samples.
2. Single-Operator Bias and Precision for Nitrate Determined from Quality Control Check Samples.

FIGURES

1. Percentile Nitrate-Nitrite Concentration Values Obtained from Wet Deposition Samples.
2. Nitrate-Nitrite Sampling and Analytical System -- Segmented Flow.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the automated colorimetric measurement of nitrate-nitrite in wet deposition samples by cadmium reduction.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a calibration standard containing 0.10 mg/L nitrate is 0.02 mg/L. The analyte concentration range of this method is 0.02-5.00 mg/L as NO_3^-.

1.4 Figure 1 represents a cumulative frequency percentile nitrate-nitrite concentration plot obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of appropriate calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 A filtered sample is mixed with ammonium chloride and introduced into a copper-cadmium reduction column. Nitrate ions are reduced to nitrite ions and mixed with a color reagent to form a reddish-purple complex. Determination of nitrite alone can be conducted by eliminating the reduction column. The intensity of the color complex is proportional to the concentration of nitrite in solution. After color development, a flowcell receives the stream for measurement. A light beam of a wavelength characteristic of the color complex is passed through the solution. The light energy measured by a photodetector is a function of the concentration of nitrite ion in the sample. Beer's Law is used to relate the measured transmittance to concentration:

$$\log(1/T) = abc$$

where: T = transmittance
a = absorptivity
b = length of light path
c = concentration of absorbing species (mg/L)

A calibration curve is constructed using standard solutions containing known concentrations of nitrate. From this curve, the concentration of nitrate-nitrite in a wet deposition sample is determined.

3. DEFINITIONS

3.1 COLORIMETRY -- the measurement of light transmitted by a colored complex as a function of concentration.

3.2 For definitions of other terms used in this method, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.1).

4. INTERFERENCES

4.1 Sample color absorbing in the wavelength range of 510-530 nm will increase the measured concentration of nitrate-nitrite in the sample. Wet deposition samples are generally colorless; therefore, this type of interference is rare. If color does cause a problem, however, a sample not containing N-(1-naphthyl)ethylenediamine Dihydrochloride can be analyzed and the measured concentration subtracted.

4.2 In this method, the volume of alkaline solution (NH_4Cl) used is 3.8 times that of the sample. This ensures that wet deposition samples with pH's as low as 3.5 are easily neutralized by the alkaline reagent and reduced properly in the cadmium column.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated hydrochloric acid (Sect. 7.8).

5.2 Use a fume hood when preparing the alkaline water (Sect. 7.3). Vapors produced by this reagent are extremely irritating.

5.3 When preparing the cadmium reduction column (Sect. 11.1), use gloves, safety glasses, protective clothing, and a fume hood. Cadmium produces nephrotoxic effects; therefore, avoid all skin and respiratory contact (14.2).

CAUTION: When discarding cadmium waste, store in a tightly sealed container for later disposal at a hazardous waste treatment/storage facility.

5.4 Follow American Chemical Society guidelines regarding safe handling of chemicals used in this method (14.3).

6. APPARATUS AND EQUIPMENT

6.1 AUTOMATED COLORIMETRIC INSTRUMENT -- Select and assemble an analytical system consisting of the following:

6.1.1 Sampler.

6.1.2 Proportioning Pump.

6.1.3 Analytical Cartridge.

6.1.3.1 Reduction column -- Use glass or flexible polyolefin tubing having a length of 36 cm with an inside diameter of 2.29 mm (0.09 inches). Prepare the reduction column according to the procedure in Sect. 11.1.

6.1.4 Colorimeter with a 520 nm wavelength setting. Ensure that the colorimeter is equipped with photodetectors having maximum sensitivity at this wavelength setting. A 15 mm flow cell is adequate to achieve the MDL stated in Sect. 1.3.

6.1.5 Strip Chart Recorder (or other data acquisiton device).

6.1.6 Printer (optional).

6.3 Wherever possible, use glass transmission lines with an inside diameter of 1.85 mm (0.073 inches) in the analytical cartridge and colorimeter. Glass yields a more uniform sample flow and does not degrade as quickly as other tubing materials. When connecting two glass lines, ensure that the lines are abutted. To minimize sample pulsing, maintain uniform inside diameter throughout all transmission tubing. Minimize the length of all transmission tubing to optimize the performance of the hydraulic system.

6.4 Enclose the sampler with a dust cover to prevent contamination.

6.5 To prevent the intake of any precipitates from the reagents, install intake filters at the end of the transmission lines that are used to transport the reagents from their respective containers to the proportioning pump.

6.6 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.4). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 ALKALINE WATER (pH 10.0) -- Add 1.8 mL of ammonium hydroxide (NH_4OH) to water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a polyolefin container.

CAUTION: Refer to Sect. 5.2 for precautions when preparing this reagent since it produces irritating vapors.

7.4 AMMONIUM CHLORIDE REAGENT (pH 8.5) -- Dissolve 10 g of ammonium chloride (NH_4Cl) in alkaline water (Sect. 7.3) and dilute to 1 L. Add 0.5 mL of a wetting agent that does not contain nitrate-nitrite, such as Brij-35.

7.5 CADMIUM -- 40 mesh, coarse granules, 99% pure.

CAUTION: Follow the precautions in Sect. 5.3 to avoid all skin and respiratory contact with the granules.

7.6 COLOR REAGENT -- Add 100 mL of concentrated phosphoric acid (H_3PO_4 sp gr 1.71), 10 g of sulfanilamide ($C_6H_8N_2O_2S$), and 0.50 g of N-(1-Naphthyl)-ethylenediamine Dihydrochloride ($C_{12}H_{14}N_2 \cdot 2HCl$) to 800 mL of water (Sect. 7.2) and dilute to 1 L. Add 0.5 mL of a wetting agent that does not contain nitrate-nitrite, such as Brij-35. This solution is stable for one month when refrigerated at 4°C in an amber glass or polyolefin container. Allow the color reagent to reach ambient temperature before use.

7.7 COPPER SULFATE SOLUTION (4.00 g/L) -- Dissolve 2.00 g of copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) in water (Sect. 7.2) and dilute to 500 mL. This solution is stable for two months when stored at room temperature in a glass or polyolefin container.

7.8 HYDROCHLORIC ACID (1.0 N) -- Add 83.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 900 mL of water (Sect. 7.2) and dilute to 1 L.

7.9 NITRATE SOLUTION, STOCK (1.0 mL = 1.0 mg NO_3) -- Dissolve 1.3707 g of sodium nitrate ($NaNO_3$), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L. This solution is stable for one year when stored at room temperature in a glass or polyolefin container.

7.10 SAMPLER RINSE WATER -- Add 0.5 mL of a wetting agent that does not contain nitrate-nitrite, such as Brij-35, to 1 L of water (Sect. 7.2).

7.11 SAMPLE CONTAINERS -- Use polyolefin sample cups or glass test tubes that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The presence of microbial activity will affect the stability of nitrate concentrations in wet deposition samples. Sample measurements should be made immediately after collection whenever possible. The biological conversion of NH_4 and nitrite (NO_2) to nitrate after sample collection can be minimized by storing samples at 4°C prior to analysis.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is partially effective at stabilizing nitrate by removal of biological species. Refrigeration after immediate filtration is the most reliable method to ensure sample integrity (14.5). Sample storage time should not exceed one week.

9. CALIBRATION AND STANDARDIZATION

9.1 INSTRUMENT OPTIMIZATION

9.1.1 For a segmented flow system with a concentration range from 0.02-5.00 mg/L as nitrate-nitrite, assemble the sampling and analytical system as shown in Figure 2.

9.1.2 Prepare and activate the reduction column according to Sect. 11.1.

9.1.3 Use flow rated polyvinyl chloride (PVC) or polyethylene pump and transmission tubing throughout the sampling and analytical system. Check the tubing for chemical buildup, splits, cracks, and deformations before beginning each day's analysis. Change pump tubes after 50 hours of operation. Change transmission tubes after 100 hours of operation or when uneven flow patterns are observed.

9.1.4 Optimize the tension of the pump tubes according to the manufacturer's recommendations.

9.1.5 Set the wavelength of the colorimeter to 520 nm. Allow the colorimeter to warm up for 30 minutes while pumping sampler rinse water (Sect. 7.10) and reagents through the system. After a stable baseline has been obtained, adjust the recorder to maximize the full-scale response.

9.1.6 Sample at a rate of 40 samples/hour with a 1:4 sample to rinse ratio. This sampling rate provides good peak separation. Adjust the colorimeter to maximize sensitivity while minimizing instrument noise. Refer to the manufacturer's recommendations.

9.2 CALIBRATION SOLUTIONS

9.2.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain nitrate at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of nitrate-nitrite in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for nitrate-nitrite are as follows: zero, 0.02, 1.25, 2.50, 3.75, and 5.00 mg/L as NO_3^-.

9.2.2 Prepare all calibration standards by diluting the stock standard (Sect. 7.9) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. Standards with nitrate concentrations greater than 0.25 mg/L are stable for one week when stored at room temperature in glass or polyolefin containers. Prepare standards with 0.25 mg/L or less of nitrate every day and store at room temperature in glass or polyolefin containers.

9.3 CALIBRATION CURVE

9.3.1 Analyze the standard containing the highest concentration of nitrate and adjust the colorimeter calibration control to obtain full-scale deflection on the recorder. Use the zero standard to adjust the baseline. If a printer is used, adjust it to read the correct concentration. Analyze all the standards and construct a calibration curve according to Sect. 12. After every 30 samples and at the end of each day's analyses, reconstruct the entire calibration curve.

9.3.2 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.5.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.6). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.4 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 2. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.7), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the nitrate concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample (QCS) after the calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the system or the calibration procedure. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.6). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 REDUCTION COLUMN

11.1.1 Wash about 5 g of cadmium granules with five 10 mL aliquots of 1.0 N HCl. Rinse with equal volumes of water (Sect. 7.2). The cadmium should be a silver color after cleaning.

11.1.2 Wash the cadmium with five 10 mL aliquots of $CuSO_4$ until colloidal copper particles form and no blue color remains. Wash the granules thoroughly with equal portions of water (Sect. 7.2) to remove the colloidal copper. The cadmium should appear black after cleaning.

11.1.3 Fill the column with water (Sect. 7.2). Add the prepared cadmium to the column and plug the open ends with 80 mesh teflon screen or glass wool.

Note: Do not allow air to enter the column or let the cadmium become dry. The presence of air bubbles reduces column efficiency. If air enters the column, repeat the above procedure.

11.1.4 Fill all pump tubes with reagents before inserting the column in the analytical stream to prevent the introduction of air bubbles. Make sure no air is present in any of the transmission lines leading to the column.

11.1.5 For initial activation of the column, continuously sample a 100 mg/L nitrate standard for five minutes. Rinse with sampler rinse water (sect. 7.10) for at least ten minutes.

11.2 A reduction column prepared according to Sect. 11.1 should last for 300-400 samples. The cadmium in the column can be reactivated and used again to prepare a new column by repeating the procedure outlined in Sect. 11.1.

11.3 Optimize the instrument each day according to Sect. 9.1.

11.4 Prepare all standards and construct a calibration curve according to Sects. 9.2 and 9.3.

11.5 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.6 Load the sampler tray and begin analysis.

11.7 If the peak height response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.8 When analysis is complete, rinse the cadmium reduction column with NH_4Cl for one minute, remove the reduction column, and seal each end of the column tubing to avoid exposure of the cadmium to air. Alternatively, the system can be equipped with a switching valve to allow the operator to take the column off-line. Rinse the remainder of the system with sampler rinse water (Sect. 7.10) for 30 minutes.

12. CALCULATIONS

12.1 Calculate a linear least squares fit of the standard concentration as a function of the measured peak height. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1x$$

where: y = standard concentration in mg/L
x = peak height measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n}(x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of peak heights measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of nitrate-nitrite from the calibration curve.

12.2 If the relationship between standard concentration and measured peak height is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of nitrate-nitrite from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of nitrate-nitrite.

12.4 If the concentration of nitrate alone is desired, determine the content of nitrite in the samples by eliminating the reduction column from the system. Subtract the nitrite from the total nitrate-nitrite concentration.

12.5 Report data in mg/L as NO_3^-. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.7). The results are summarized in Table 1. No statistically significant biases were found.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 2.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.2 "Trace Metals in Water Supplies: Occurrence, Significance, and Control," American Water Works Association, Illinois Environmental Protection Agency, **Vol. 71**, No. 108, April 29, 1974.

14.3 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.4 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.5 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. **12**, 1978, pp. 2343-2349.

14.6 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.7 Annual Book of ASTM Standards, Section 11, **Vol. 11.01 (1)**, "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Single-Operator Precision and Bias for Nitrate-Nitrite Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Nitrate	0.56	9	94.5	-0.03	0.03	No
	1.21	10	96.3	-0.04	0.03	No

a. Number of replicates
b. 95% Confidence Level

Table 2. Single-Operator Precision and Bias for Nitrate Determined from Quality Control Check Samples.

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
0.62	0.63	88	0.01	1.6	0.02	3.2
0.80	0.78	24	-0.02	-2.5	0.01	1.3
3.17	3.11	88	-0.06	-1.9	0.07	2.2
3.54	3.44	23	-0.10	-2.8	0.05	1.4

The above data were obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

a. Number of replicates

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Nitrate-Nitrite

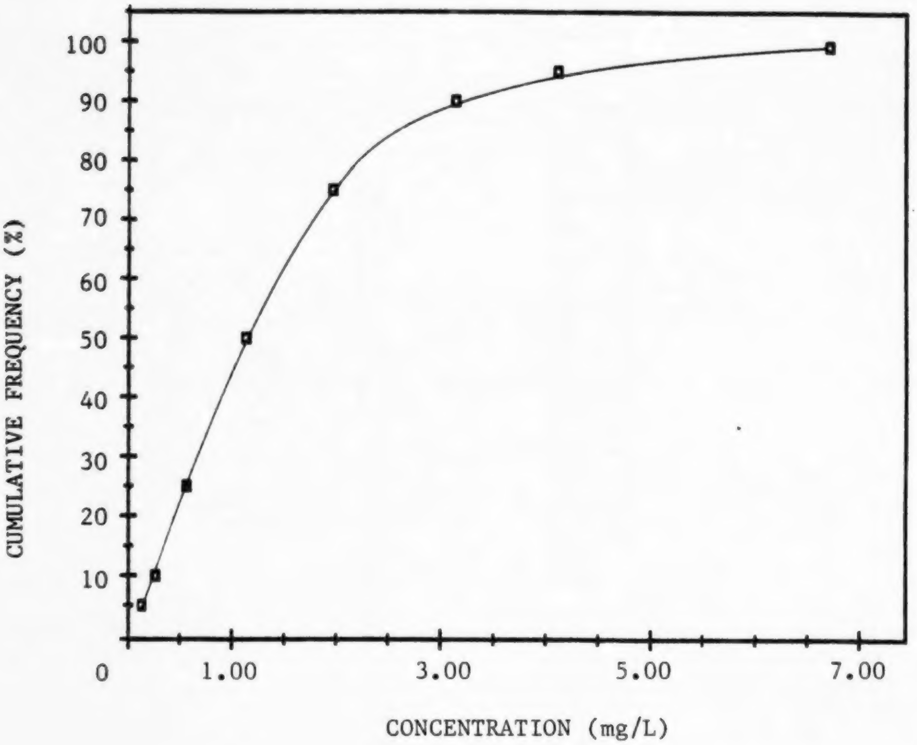
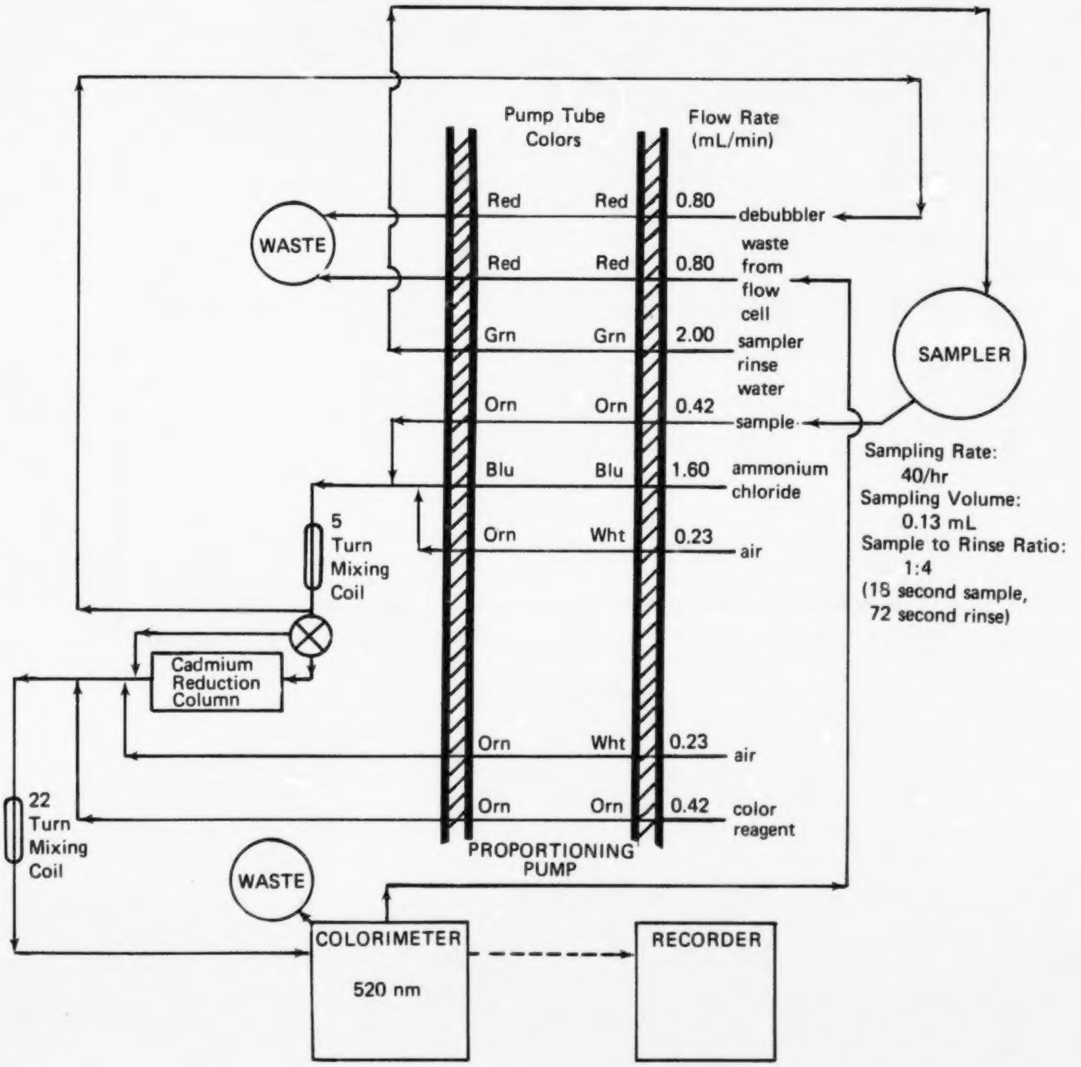


Figure 2. Nitrate-Nitrite Sampling and Analytical System -- Segmented Flow.


Pump Tube Colors
Flow Rate (mL/min)
Red
Red
0.80
debubbler
WASTE
Red
Red
0.80
waste from flow cell
Grn
Grn
2.00
sampler rinse water
SAMPLER
Orn
Orn
0.42
sample
Blu
Blu
1.60
ammonium chloride
Orn
Wht
0.23
air
Sampling Rate: 40/hr
Sampling Volume: 0.13 mL
Sample to Rinse Ratio: 1:4
(18 second sample, 72 second rinse)
5 Turn Mixing Coil
Cadmium Reduction Column
Orn
Wht
0.23
air
Orn
Orn
0.42
color reagent
22 Turn Mixing Coil
PROPORTIONING PUMP
WASTE
COLORIMETER
520 nm
RECORDER

Method 365.6 -- Orthophosphate in Wet Deposition by Automated Colorimetric Determination Using Ascorbic Acid Reduction

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Performing Laboratory:

Susan R. Bachman
Michael J. Slater
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Single-Operator Precision and Bias for Orthophosphate Determined from Analyte Spikes of Wet Deposition Samples.
2. Single-Operator Bias and Precision for Orthophosphate Determined from Quality Control Check Samples.

FIGURES

1. Orthophosphate Sampling and Analytical System -- Segmented Flow.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the automated colorimetric determination of orthophosphate in wet deposition samples by ascorbic acid reduction.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a calibration standard containing 0.03 mg/L orthophosphate is 0.02 mg/L. The concentration range of this method is 0.02-0.25 mg/L as PO_4^{-3}.

1.4 The maximum concentration of phosphate observed from analyses of over five thousand wet deposition samples was 12.60 mg/L. Over 90% of the samples, however, had phosphate concentrations below the MDL.

2. SUMMARY OF METHOD

2.1 A filtered sample is mixed with an acidified solution of ammonium molybdate containing ascorbic acid and antimony to form a phosphomolybdenum blue complex. The intensity of the color complex is proportional to the concentration of orthophosphate in solution. The solution is pumped through a 37°C controlled temperature heating bath. After color development, a flowcell receives the stream for measurement. A light beam of a wavelength characteristic of the phosphomolybdenum blue complex is passed through the solution. The light energy measured by a photodetector is a function of the concentration of orthophosphate ion in the sample. Beer's Law is used to relate the measured transmittance to concentration:

$$\log(1/T) = abc$$

where: T = transmittance
a = absorptivity
b = length of light path
c = concentration of absorbing species (mg/L)

A calibration curve is constructed using standard solutions containing known concentrations of orthophosphate. From this curve, the concentration of orthophosphate in a wet deposition sample is determined.

3. DEFINITIONS

3.1 COLORIMETRY -- the measurement of light transmitted by a colored complex as a function of concentration.

3.2 For definitions of other terms used in these methods, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.1).

4. INTERFERENCES

4.1 Sample color absorbing in the wavelength range of 870-890 nm will increase the measured concentration of orthophosphate in the sample. Wet deposition samples are generally colorless, therefore, this type of interference is rare.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated hydrochloric acid (Sect. 7.6) and sulfuric acid (Sect. 7.8).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.2).

6. APPARATUS AND EQUIPMENT

6.1 AUTOMATED COLORIMETRIC INSTRUMENT -- Select and assemble an analytical system consisting of the following:

6.1.1 Sampler.

6.1.2 Proportioning Pump.

6.1.3 Analytical Cartridge.

6.1.4 Heating Bath (37°C) equipped with an 8 mL capacity glass heating coil.

6.1.5 Colorimeter with an 880 nm wavelength setting. Ensure that the colorimeter is equipped with photodetectors having maximum sensitivity at this wavelength setting. A 50 mm flow cell is required to achieve the MDL stated in Sect. 1.3.

6.1.6 Strip Chart Recorder (or other data acquisition device).

6.1.7 Printer (optional).

6.2 Wherever possible, use glass transmission lines in the analytical cartridge and colorimeter. Glass yields a more uniform sample flow and does not degrade as quickly as other tubing materials. When connecting two glass lines, ensure that the ends are abutted. To minimize pulsing of the analytical stream, maintain uniform inside diameter throughout all transmission tubing. Flexible transmission tubing should have an inside diameter of 1.3 mm (0.051 inches). Minimize the length of all transmission tubing to optimize the performance of the hydraulic system.

6.3 Enclose the sampler with a dust cover to prevent contamination.

6.4 To prevent the intake of any precipitates from the reagents, install intake filters at the end of the transmission lines that are used to transport the reagents from their respective containers to the proportioning pump.

6.5 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.3). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 AMMONIUM MOLYBDATE SOLUTION -- Dissolve 40 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container.

7.4 ANTIMONY POTASSIUM TARTRATE SOLUTION -- Dissolve 3 g of antimony potassium tartrate ($K(SbO)C_4H_4O_6\cdot 1/2H_2O$) in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container.

7.5 ASCORBIC ACID SOLUTION -- Dissolve 9.0 g of ascorbic acid ($C_6H_8O_6$) in water (Sect. 7.2) and dilute to 500 mL. This solution is stable for two weeks when refrigerated at 4°C in a high density polyethylene or polypropylene container.

7.6 HYDROCHLORIC ACID (1.0 N) -- Add 83.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 900 mL of water (Sect. 7.2) and dilute to 1 L.

7.7 ORTHOPHOSPHATE SOLUTION, STOCK (1.0 mL = 0.1 mg PO_4) -- Dissolve 143.47 mg of potassium phosphate (KH_2PO_4), dried at 105°C for one hour, in water (Sect. 7.2). Add 1 mL of chloroform ($CHCl_3$) and dilute to 1 L with water (Sect. 7.2). This solution is stable for one year when stored in a glass or a high density polyethylene or polypropylene container at 4°C.

7.8 SULFURIC ACID (4.9 N) -- Add 136 mL of concentrated sulfuric acid (H_2SO_4 sp gr 1.84) to 800 mL of water (Sect. 7.2). Allow the solution to cool and dilute to 1 L.

7.9 COLOR REAGENT -- Allow all solutions to reach room temperature before combining as follows: to 50 mL of sulfuric acid add 15 mL of ammonium molybdate solution, 30 mL of ascorbic acid solution, and 5 mL of antimony potassium tartrate solution. Add approximately 50 uL of Levor V or a similar wetting agent that does not contain orthophosphate. The color reagent will remain relatively stable in a high density polyethylene or polypropylene container for eight hours. This reagent does, however, slowly degrade over an eight hour period resulting in decreased sensitivity. To better preserve the reagent, place the container in an ice water bath while analyzing samples.

7.10 SAMPLE CONTAINERS -- Use polyolefin sample cups or glass test tubes that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The presence of microbial activity will affect the stability of orthophosphate concentrations in wet deposition samples. Sample measurements should be made immediately after collection whenever possible.

8.3.1 Filtration of samples through a 0.45 micrometer membrane leached with water (Sect. 7.2) is partially effective at stabilizing orthophosphate by removal of biological species. Refrigeration after immediate filtration is the most reliable method to ensure sample integrity (14.4). Sample storage time should not exceed one week.

9. CALIBRATION AND STANDARDIZATION

9.1 INSTRUMENT OPTIMIZATION

9.1.1 For a flow segmented system with a concentration range from 0.02-0.25 mg/L as orthophosphate, assemble the sampling and analytical system as shown in Figure 1.

9.1.2 Use flow rated polyvinyl chloride or polyethylene pump and transmission tubing throughout the sampling and analytical system. Check the tubing for chemical buildup, splits, cracks, and deformations before beginning each day's analysis. Change pump tubes after 25 hours of operation. Change transmission tubing after 50 hours of operation or when uneven flow patterns are observed.

9.1.3 Optimize the tension of the pump tubes according to manufacturer's recommendations.

9.1.4 Set the heating bath to 37°C. Set the wavelength of the colorimeter to 880 nm. Allow the colorimeter and heating bath to warm up for 30 minutes while pumping water (Sect. 7.2) and color reagent through the system. After a a stable baseline has been obtained, adjust the recorder to maximize the full-scale response.

9.1.5 Sample at a rate of 30 samples/hour with a 1:4 sample to rinse ratio. This sampling rate provides good peak separation. Adjust the colorimeter to maximize sensitivity while minimizing instrument noise. Refer to the manufacturer's recommendations.

9.2 CALIBRATION SOLUTIONS

9.2.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain orthophosphate at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of orthophosphate in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for orthophosphate are as follows: zero, 0.02, 0.04, 0.06, 0.08, and 0.10 mg/L as PO_4^{-3}.

9.2.2 Prepare all calibration standards by diluting the stock solution (Sect. 7.7) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. Standards with a concentration greater than 0.04 mg/L orthophosphate are stable for one week if stored at room temperature in high density polyethylene or polypropylene containers. Prepare standards with 0.04 mg/L or less orthophosphate every day and store at room temperature in high density polyethylene or polypropylene containers.

9.3 CALIBRATION CURVE

9.3.1 Analyze the standard containing the highest concentration of orthophosphate and adjust the colorimeter calibration control to obtain full-scale deflection on the recorder. If a printer is used, adjust it to read the correct concentration. Analyze all the standards and construct a calibration curve according to Sect. 12. After every 30 samples and at the end of the day's analyses, reconstruct the entire calibration curve.

9.3.2 Verify the calibration curve after every ten samples and at the end of each day's analyses according to Sect. 10.5.

10. QUALITY CONTROL

10.1 Each laboratory using this method should develop formalized quality control protocols to continually monitor the bias and precision of all measurements. These protocols are required to ensure that the measurement system is in a state of statistical control. Estimates of bias and precision for wet deposition analyses cannot be made unless these control procedures are followed. Detailed guidelines for the development of quality assurance and quality control protocols for wet deposition measurement systems are published in a manual available from the United States Environmental Protection Agency, Research Triangle Park, NC 27711 (14.5). Included in this manual are procedures for the development of statistical control charts for use in monitoring bias and precision as well as recommendations for the introduction of reagent blanks, laboratory duplicates, field duplicates, spike samples, and performance evaluation samples. These guidelines are to be used by all laboratories involved with wet deposition measurements.

10.2 ESTABLISHMENT OF WARNING AND CONTROL LIMITS -- Warning and control limits are used to monitor drift in the calibration curve, analyses of quality control check samples (QCS), and measured recoveries from laboratory spikes.

10.2.1 Calibration Curve -- After a calibration curve has been constructed according to Sect. 12, reanalyze additional aliquots of the low and high concentration standards. Calculate the concentrations using the previously derived calibration curve. Repeat this procedure until at least ten determinations at each concentration level have been made. These data should be collected on ten different days to provide a realistic estimate of the method variability. Calculate a standard deviation (s) at each concentration level. Use the nominal standard concentration as the mean value ($\bar{x}$) for determining the control limits. A warning limit of $\bar{x} \pm 2s$ and a control limit of $\bar{x} \pm 3s$ should be used. Reestablish these limits whenever instrumental operating conditions change.

10.2.2 Quality Control Check Samples (QCS) -- Calculate warning and control limits for QCS solutions from a minimum of ten analyses performed on ten days. Use the calculated standard deviation (s) at each QCS concentration level to develop the limits as described in Sect. 10.2.1. Use the certified or NBS traceable concentration as the mean (target) value. Constant positive or negative measurements with respect to the true value are indicative of a method or procedural bias. Utilize the data obtained from QCS measurements as in Sect. 10.4 to determine when the measurement system is out of statistical control. The standard deviations used to generate the QCS control limits should be comparable to the single operator precision reported in Table 2. Reestablish new warning and control limits whenever instrumental operating conditions are varied or QCS concentrations are changed.

10.2.3 Laboratory Spike Solutions -- A minimum of ten analyte spikes of wet deposition samples is required to develop a preliminary data base for the calculation of warning and control limits for spike recovery data. Select the spike concentration such that the working range of the method will not be exceeded. Samples selected for the initial spike recovery study should represent the concentration range common to wet deposition samples in order to reliably estimate the method accuracy. Calculate a mean and standard deviation of the percent recovery data using the formulas provided in the glossary. Determine warning and control limits using $\pm 2s$ and $\pm 3s$, respectively. If the data indicate that no significant method bias exists (14.6), the 100 percent recovery is used as the mean percent recovery. Where a significant bias is determined at the 95% confidence level, the control limits are centered around the bias estimate. Routine spiked sample analyses that yield percent recovery data outside of the control limits are an indication of matrix interferences that should be resolved before routine analyses are continued.

10.2.4 All warning and control limits should be reevaluated on a continual basis as additional data are collected during routine analyses. The limits should be broadened or narrowed if a recalculated standard deviation under similar operating conditions provides a different estimate of the procedure variability.

10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the orthophosphate concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample (QCS) after the calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the system or the calibration procedure. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.5). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 Optimize the instrument each day according to Sect. 9.1.

11.2 Prepare all standards and construct a calibration curve according to Sect. 9.2 and 9.3.

11.3 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.4 Load the sampler tray and begin analysis.

11.5 If the peak height response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.6 When analysis is complete, turn off the heating bath and rinse the system with 1 N HCl for 15 minutes. Rinse the system with water (Sect. 7.2) for an additional 15 minutes.

12. CALCULATIONS

12.1 Calculate a linear least squares fit of the standard concentration as a function of the measured peak height. The linear least squares equation is expressed as follows:

$$y = B_0 + B_1x$$

where: y = standard concentration in mg/L
x = peak height measured
B_0 = y-intercept calculated from: $\bar{y} - B_1\bar{x}$
B_1 = slope calculated from:

$$\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y}) / \sum_{i=1}^{n}(x_i - \bar{x})^2$$

where: $\bar{x}$ = mean of peak heights measured
$\bar{y}$ = mean of standard concentrations
n = number of samples

The correlation coefficient should be 0.9990 or greater. Determine the concentration of analyte of interest from the calibration curve.

12.2 If the relationship between standard concentration and measured peak height is nonlinear, use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of orthophosphate from the calibration curve.

12.3 An integration system may also be used to provide a direct readout of the concentration of orthophosphate.

12.4 Report data in mg/L as PO_4^{-3}. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.6). The results are summarized in Table 1. A small but statistically significant bias of -0.01 mg/L was found at both spike concentration levels.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 2.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.2 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.3 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.4 Peden, M. E. and Skowron, L. M., "Ionic Stability of Precipitation Samples," Atmos. Environ. **12**, 1978, pp. 2343-2349.

14.5 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.6 Annual Book of ASTM Standards, Section 11, **Vol. 11.01 (1)**, "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Single-Operator Precision and Bias for Orthophosphate Determined from Analyte Spikes of Wet Deposition Samples.[a]

Analyte	Amount Added, mg/L	n[b]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[c]
Ortho-phosphate	0.061	10	81.0	-0.012	0.002	Yes
	0.159	9	92.7	-0.012	0.004	Yes

a. Concentration values are significant to two decimal places.
b. Number of replicates
c. 95% Confidence Level

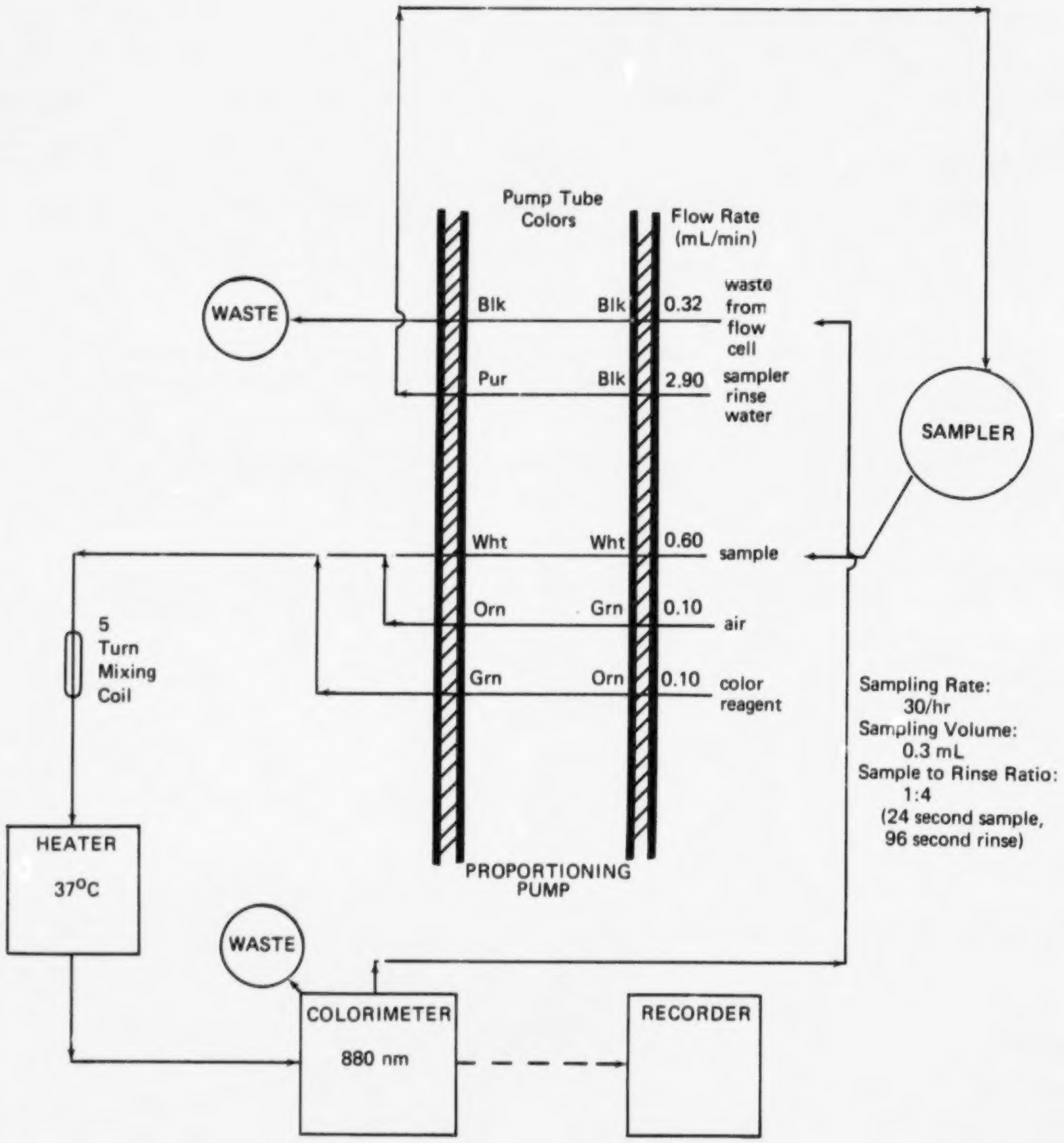
Table 2. Single-Operator Bias and Precision for Orthophosphate Determined from Quality Control Check Samples.[a]

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[b]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
0.031	0.026	151	-0.005	-16.1	0.007	26.9
0.062	0.055	161	-0.007	-11.3	0.008	14.5
0.123	0.117	84	-0.006	-4.9	0.006	5.1
0.215	0.205	74	-0.010	-4.6	0.010	4.9

The above data were obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

a. Concentration values are significant to two decimal places.
b. Number of replicates

Figure 1. Orthophosphate Sampling and Analytical System -- Segmented Flow.


Pump Tube Colors
Flow Rate (mL/min)
WASTE
Blk
Blk
0.32
waste from flow cell
Pur
Blk
2.90
sampler rinse water
SAMPLER
Wht
Wht
0.60
sample
Orn
Grn
0.10
air
Grn
Orn
0.10
color reagent
5 Turn Mixing Coil
Sampling Rate: 30/hr
Sampling Volume: 0.3 mL
Sample to Rinse Ratio: 1:4
(24 second sample, 96 second rinse)
HEATER
37°C
PROPORTIONING PUMP
WASTE
COLORIMETER
880 nm
RECORDER

Method 375.6 -- Sulfate in Wet Deposition by Automated Colorimetric Determination Using Barium-Methylthymol Blue

March 1986

Performing Laboratory:

Susan R. Bachman
Michael J. Slater
Carla Jo Brennan
Mark E. Peden

Illinois State Water Survey
Analytical Chemistry Unit
2204 Griffith Drive
Champaign, Illinois 61820

Sponsoring Agency:

John D. Pfaff, Project Officer

Inorganic Analysis Section
Physical and Chemical Methods Branch
United States Environmental Protection Agency
Office of Research and Development
Environmental Monitoring and Support Laboratory
Cincinnati, Ohio 45268

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TABLES

1. Single-Operator Precision and Bias for Sulfate Determined from Analyte Spikes of Wet Deposition Samples.
2. Single-Operator Bias and Precision for Sulfate Determined from Quality Control Check Samples.

FIGURES

1. Percentile Concentration Values Obtained from Wet Deposition Samples: Sulfate.
2. Sulfate Sampling and Analytical System -- Segmented Flow.

1. SCOPE AND APPLICATION

1.1 This method is applicable to the automated colorimetric determination of sulfate in wet deposition samples by barium-methylthymol blue reaction.

1.2 The term "wet deposition" is used in this method to designate rain, snow, dew, sleet, and hail.

1.3 The method detection limit (MDL) determined from replicate analyses of a quality control check solution containing 0.36 mg/L sulfate is 0.05 mg/L. The concentration range of this method is 0.05-6.00 mg/L as SO_4^{-2}.

1.4 Figure 1 represents a cumulative frequency percentile sulfate concentration plot obtained from analyses of over five thousand wet deposition samples. These data may be used as an aid in the selection of calibration standard concentrations.

2. SUMMARY OF METHOD

2.1 A sample is pumped through an ion exchange column for the removal of interfering cations, and then reacted with barium chloride at pH 2.5-3.0 to form barium sulfate. To enhance the complexation of barium with methylthymol blue (MTB), sodium hydroxide is added to increase the pH to approximately 12.5. Excess barium ions react with an equivalent concentration of MTB to form a blue-colored chelate. The concentration of unchelated MTB ions is related to the initial sulfate ion concentration. Therefore, the intensity of the blue-colored chelate is inversely proportional to the concentration of sulfate in solution. After color reduction, a flowcell receives the stream for measurement. A light beam of a wavelength characteristic of the blue-colored chelate is passed through the solution. The light energy measured by a photodetector is inversely related to the concentration of sulfate in the sample. A calibration curve is constructed using standard solutions containing known concentrations of sulfate. From this curve, the concentration of sulfate in a wet deposition sample is determined.

3. DEFINITIONS

3.1 COLORIMETRY -- the measurement of light transmitted by a colored complex as a function of concentration.

3.2 ION EXCHANGE -- a reversible process by which ions are interchanged between an insoluble material and a liquid with no substantial structural changes of the material (14.1).

3.3 For definitions of other terms used in these methods, refer to the glossary. For an explanation of the metric system including units, symbols, and conversion factors see American Society for Testing and Materials (ASTM) Standard E 380, "Metric Practices" (14.2).

4. INTERFERENCES

4.1 Sample color absorbing in the wavelength range of 450-470 nm will reduce the measured concentration of sulfate in the sample. Wet deposition samples are generally colorless, therefore, this type of interference is rare.

4.2 Phosphate at concentrations as low as 0.01 mg/L will complex with the methylthymol blue reagent to result in a positive bias. Sulfite may be oxidized to sulfate to yield a positive bias.

4.3 Cations such as calcium, aluminum, and iron that may also interfere by complexing with the methylthymol blue reagent are removed by the ion exchange column. If the ion exchange column capacity is exceeded, the interfering cations are not completely removed and a new column must be prepared.

4.4 The presence of air bubbles in the ion exchange column results in incomplete removal of the interfering cations and is evidenced by an unstable baseline. Eliminate this interference by preparing the column carefully in accordance with the details provided in Sect. 11.1.

5. SAFETY

5.1 The calibration standards, sample types, and most reagents used in this method pose no hazard to the analyst. Use a fume hood, protective clothing, and safety glasses when handling concentrated hydrochloric acid (Sect. 7.5) and sodium hydroxide (Sect. 7.9).

5.2 Follow American Chemical Society guidelines regarding the safe handling of chemicals used in this method (14.3).

6. APPARATUS AND EQUIPMENT

6.1 AUTOMATED COLORIMETRIC INSTRUMENT -- Select and assemble an analytical system consisting of the following:

6.1.1 Sampler.

6.1.2 Proportioning Pump.

6.1.3 Analytical Cartridge.

6.1.3.1 Ion Exchange Column -- Flexible polyolefin tubing or glass tubing having a length of 15 to 20 cm with an inside diameter equal to the tubing in the rest of the system. Prepare the ion exchange column according to the procedure in Sect. 11.1.

6.1.4 Colorimeter with a 460 nm wavelength setting. Ensure that the colorimeter is equipped with photodetectors having maximum sensitivity at this wavelength setting. A 15 mm flow cell is adequate to achieve the MDL stated in Sect. 1.3. A 50 mm flow cell may be selected to increase sensitivity.

6.1.5 Strip Chart Recorder (or other data acquisition device).

6.1.6 Printer (optional).

6.2 Wherever possible, use glass transmission lines with an inside diameter of 1.85 mm (0.073 inches) in the analytical cartridge and colorimeter. Glass yields a more uniform sample flow and does not degrade as quickly as other tubing materials. When connecting two glass lines, ensure that the ends are abutted. To minimize pulsing of the analytical stream, maintain uniform inside diameter throughout all transmission tubing. Minimize the length of all transmission tubing to optimize the performance of the hydraulic system.

6.4 Enclose the sampler with a dust cover to prevent contamination.

6.5 To prevent the intake of any precipitates from the reagents, install intake filters at the end of the transmission lines that are used to transport the reagents from their respective containers to the proportioning pump.

6.6 LABORATORY FACILITIES -- Laboratories used for the analysis of wet deposition samples should be free from external sources of contamination. The use of laminar flow clean air workstations is recommended for sample processing and preparation to avoid the introduction of airborne contaminants. Samples should always be capped or covered prior to analysis. A positive pressure environment within the laboratory is also recommended to minimize the introduction of external sources of contaminant gases and particulates. Windows within the laboratory should be kept closed at all times and sealed if air leaks are apparent. The use of disposable tacky floor mats at the entrance to the laboratory is helpful in reducing the particulate loading within the room.

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 PURITY OF REAGENTS -- Use reagent grade chemicals for all solutions. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS), where such specifications are available.

7.2 PURITY OF WATER -- Use water conforming to ASTM Specification D 1193, Type II (14.4). Point of use 0.2 micrometer filters are recommended for all faucets supplying water to prevent the introduction of bacteria and/or ion exchange resins into reagents, standard solutions, and internally formulated quality control check solutions.

7.3 BARIUM CHLORIDE SOLUTION -- Dissolve 1.526 g of barium chloride ($BaCl_2 \cdot H_2O$) in water (Sect. 7.2) and dilute to 1 L. Store at room temperature in an amber high density polyethylene or polypropylene container.

7.4 ETHANOL (C_2H_5OH, Et-OH) -- 95% volume/volume.

7.5 HYDROCHLORIC ACID (1.0 N) -- Add 83.0 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 900 mL of water (Sect. 7.2) and dilute to 1 L.

7.6 ION EXCHANGE RESIN -- Analytical grade carboxylic cation exchange resin with a 20 to 50 mesh; sodium form.

7.7 METHYLTHYMOL BLUE REAGENT (MTB) -- Add 25 mL of the barium chloride solution to 0.1182 g of methylthymol blue (3'3"-Bis-N, N-bis (carboxymethyl)- amino methylthymolsulfonephthalein pentasodium salt). Add 4 mL of 1 N HCl to the solution, mix well, add 71 mL of water (Sect. 7.2) , and 0.5 mL of Brij-35 or a similar wetting agent. Mix and dilute to 500 mL with 95% EtOH. Prepare daily.

7.8 SAMPLER RINSE WATER -- Add 0.5 mL Brij-35 or a similar wetting agent to 1 L of water (Sect. 7.2).

7.9 SODIUM HYDROXIDE SOLUTION (0.18 N) -- Dissolve 7.2 g of sodium hydroxide (NaOH) in 900 mL of water (sect. 7.2), add 0.5 mL of Brij-35 or a similar wetting agent and dilute to 1 L. Store at room temperature in a high density polyethylene or polypropylene container.

7.10 SULFATE SOLUTION, STOCK (1.0 mL = 1.0 mg SO_4) -- The stock solution may be purchased as a certified solution or prepared from ACS reagent grade materials. To prepare, dissolve 1.4789 g of sodium sulfate (Na_2SO_4), dried at 105°C for one hour, in water (Sect. 7.2) and dilute to 1 L. This solutions is stable for one year when stored in a high density polyethylene or polypropylene container at 4°C.

7.11 SAMPLE CONTAINERS -- Use polyolefin sample cups or glass test tubes that have been rinsed thoroughly with water (Sect. 7.2) before use.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Collect samples in high density polyethylene (HDPE) containers that have been thoroughly rinsed with ASTM Type II water (7.2). Do not use strong mineral acids or alkaline detergent solutions for cleaning collection vessels. Residual acids may remain in the polyethylene matrix and slowly leach back into the sample. Alkaline detergents may also leave residues that may affect the sample chemistry. Cap collection bottles after cleaning to prevent contamination from airborne contaminants; air dry collection buckets in a laminar flow clean air workstation and wrap in polyethylene bags prior to use. If a laminar flow workstation is not available, pour out any residual rinse water and bag the buckets immediately. Do not dry the bucket interior by any method other than air drying in a laminar flow clean air workstation.

8.2 The frequency of sample collection and the choice of sampler design are dependent on the monitoring objectives. In general, the use of wet-only samplers is recommended to exclude dry deposition contributions, minimize sample contamination, retard evaporation, and enhance sample stability. Sample collection frequency may vary from subevent to monthly sampling periods. Collection periods of more than one week are not recommended since sample integrity may be compromised by longer exposure periods.

8.3 The oxidation of sulfite to sulfate after sample collection will increase the concentration of SO_4^{-2} in stored samples. Sample measurements should be made immediately after collection if possible. Refrigeration of samples at 4°C will minimize, but not eliminate concentration changes prior to chemical analysis.

9. CALIBRATION AND STANDARDIZATION

9.1 INSTRUMENT OPTIMIZATION

9.1.1 For a segmented flow system with a concentration range from 0.05-6.00 mg/L as sulfate, assemble the sampling and analytical system as shown in Figure 2.

9.1.2 Prepare the ion exchange column according to Sect. 11.1.

9.1.3 Silicone is more resistant to the effects of ethanol, therefore, use flow rated silicone transmission and pump tubing to transport the methylthymol blue reagent from the reagent source to the analytical stream. Use silicone tubing to transport the sample from the flow cell through the pump and to waste. Elsewhere, use flow rated polyvinyl chloride or polyethylene pump and transmission tubing throughout the sampling and analytical system. Check the tubing for chemical buildup, splits, cracks, and deformations before beginning each day's analysis. Change pump tubes after 50 hours of operation. Change transmission tubing after 100 hours of operation or when uneven flow patterns are observed.

9.1.4 Optimize the tension of pump tubes according to manufacturer's recommendations.

9.1.5 Set the wavelength of the colorimeter to 460 nm. Allow the colorimeter to warm up for 30 minutes while pumping sampler rinse water and reagents through the system. After a stable baseline has been obtained, adjust the recorder to maximize the full-scale response.

9.1.6 Sample at a rate of 30 samples/hour with a 1:4 sample to rinse ratio. This sampling rate provides good peak separation. Adjust the colorimeter to maximize sensitivity while minimizing instrument noise. Refer to the manufacturer's recommendations.

9.2 CALIBRATION SOLUTIONS

9.2.1 Five calibration solutions and one zero standard are needed to generate a suitable calibration curve. The lowest calibration solution should contain sulfate at a concentration greater than or equal to the method detection limit. The highest solution should approach the expected upper limit of concentration of sulfate in wet deposition. Prepare the remaining solutions such that they are evenly distributed throughout the concentration range. Suggested calibration standards for sulfate are as follows: zero, 0.05, 1.50, 3.00, 4.50, and 6.00 mg/L as SO_4^{-2}.

9.2.2 Prepare all calibration standards by diluting the stock standard (Sect. 7.10) with water (Sect. 7.2). Use glass (Class A) or plastic pipettes that are within the bias and precision tolerances specified by the manufacturer. The standards are stable for one month if stored at room temperature in high density polyethylene or polypropylene containers.

9.3 CALIBRATION CURVE

9.3.1 Analyze the standard containing the highest concentration of sulfate and adjust the colorimeter calibration control to achieve full-scale deflection on the recorder. Use the zero standard to establish a baseline. If a printer is used, adjust it to read the correct concentration. Analyze all the standards and construct a calibration curve according to Sect. 12. After every 30 samples and at the end of the day's analyses, reconstruct the entire calibration curve.

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10.3 Monitor the cleaning procedure by pouring a volume of water (Sect. 7.2) that approximates the median sample size into the collection vessel. Allow the water to remain in the sealed or capped collection container for at least 24 hours and determine the sulfate concentration. If the solution concentration exceeds the MDL, a contamination problem is indicated in the cleaning procedure. Take corrective action before the sampling containers are used for the collection of wet deposition.

10.4 Analyze a quality control check sample (QCS) after the calibration curve has been established. This sample may be formulated in the laboratory or obtained from the National Bureau of Standards (NBS Standard Reference Material 2694, Simulated Rainwater). Verify the accuracy of internally formulated QCS solutions with an NBS traceable standard before acceptance as a quality control check. The check sample(s) selected must be within the range of the calibration standards. If the measured value for the QCS falls outside of the ±3s limits (Sect. 10.2.2), or if two successive QCS checks are outside of the ±2s limits, a problem is indicated with the system or the calibration procedure. Corrective action should be initiated to bring the results of the QCS within the established control limits. Plot the data obtained from the QCS checks on a control chart for routine assessments of bias and precision.

10.5 Verify the calibration curve after a maximum of ten samples and at the end of each day's analyses. Analyze calibration standards at the low and high ends of the working range. If the routine calibration checks do not meet the criteria described in Sect. 10.4, recalibrate the system and reanalyze all samples from the last time the system was in control. Verify the new calibration curve with the QCS according to Sect. 10.4 and reanalyze all samples measured since the last time the system was in control.

10.6 Submit a Field Blank (FB) to the laboratory for every 20 samples. The FB may consist of a water sample (Sect. 7.2) or a known reference solution that approximates the concentration levels characteristic of wet deposition. The FB is poured into the sampling vessel at the field site and undergoes identical processing and analytical protocols as the wet deposition sample(s). Use the analytical data obtained from the FB to determine any contamination introduced in the field and laboratory handling procedures. The data from the known reference solution can be used to calculate a system precision and bias.

10.7 Prepare and analyze a laboratory spike of a wet deposition sample according to the guidelines provided in "Quality Assurance Manual for Precipitation Measurement Systems" (14.5). Compare the results obtained from spiked samples to those obtained from identical samples to which no spikes were added. Use these data to monitor the method percent recovery as described in Sect. 10.2.3.

10.8 Participation in performance evaluation studies is recommended for wet deposition chemistry laboratories. The samples used for these performance audits should contain the analytes of interest at concentrations within the normal working range of the method. The true values are unknown to the analyst. Performance evaluation studies for wet deposition chemistry laboratories are conducted semiannually by the USEPA Performance Evaluation Branch, Quality Assurance Division, Research Triangle Park, NC 27711.

11. PROCEDURE

11.1 ION EXCHANGE COLUMN

11.1.1 Soak the ion exchange resin overnight in water (Sect. 7.2). Stir the slurry and decant particles smaller than 50 mesh. Store the resin in water (Sect. 7.2) in a glass or polyolefin container until the column is prepared.

11.1.2 Insert a small plug of teflon screen in one end of the column tube. To prevent the entrapment of air bubbles, fill the column with resin using a syringe or pipette attached to the same tube end and draw the resin and water mixture into the tube.

11.1.3 Do not allow air to enter the column. Do not let the resin dehydrate. Air bubbles entering the analytical stream will result in an unstable baseline. If air enters the column, repeat the procedure from Sect. 11.1.2.

11.1.4 To prevent the introduction of air, insert the column in the analytical stream while the system is pumping.

11.1.5 Prepare the column daily or whenever air enters the column.

11.2 Optimize the instrument each day according to Sect. 9.1.

11.3 Prepare all standards and construct a calibration curve according to Sect. 9.2 and 9.3.

11.4 After the calibration curve is established, analyze the QCS. If the measured value for the QCS is not within the specified limits (Sect. 10.2.2), refer to Sect. 10.4.

11.5 Load the sampler tray and begin analysis.

11.6 If the peak height response exceeds the working range of the system, dilute the sample with zero standard and reanalyze.

11.7 When analysis is complete, rinse the system with sampler rinse water (Sect. 7.8) for 15 minutes. Before changing the pump tubes, rinse a dilute concentration of HCl (1.0 N) through the system for 15 minutes to clean the mixing coils and flow cell. If the baseline appears unstable or sensitivity decreases it may be necessary to repeat this procedure more often than after 50 hours of operation.

12. CALCULATIONS

12.1 The relationship between standard concentration and measured peak height for sulfate deviates from Beer's Law. Use a second degree polynomial least squares equation to derive a curve with a correlation ≥ 0.9990. The second degree polynomial equation is expressed as follows:

$$y = B_2x^2 + B_1x + B_0$$

A computer is necessary for the derivation of this function. Determine the concentration of sulfate from the calibration curve.

12.2 An integration system may also be used to provide a direct readout of the concentration of sulfate.

12.3 Report data in mg/L as SO_4^{-2}. Do not report data lower than the lowest calibration standard.

13. PRECISION AND BIAS

13.1 The mean percent recovery and mean bias of this method were determined from the analysis of spiked wet deposition samples according to ASTM Standard Practice D4210, Annex A4 (14.6). The results are summarized in Table 1. No statistically significant biases were found.

13.2 Single-operator precision and bias were obtained from the analysis of quality control check samples that approximated the levels common to wet deposition samples. These results reflect the accuracy that can be expected when the method is used by a competent operator. These data are presented in Table 2.

14. REFERENCES

14.1 Annual Book of ASTM Standards, Part 31, "Definitions of Terms Relating to Water," Standard D 1129-82b, 1982, p. 5.

14.2 Annual Book of ASTM Standards, Part 31, "Excerpts from Standard for Metric Practice," Standard E 380-79, 1982, pp. 679-694.

14.3 "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

14.4 Annual Book of ASTM Standards, Part 31, "Standard Specification for Reagent Water," Standard D 1193-77, 1982, p. 39.

14.5 Topol, L. E., Lev-On, M., Flanagan, J., Schwall, R. J., Jackson, A. E., Quality Assurance Manual for Precipitation Measurement Systems, 1985, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC 27711.

14.6 Annual Book of ASTM Standards, Section 11, **Vol. 11.01 (1)**, "Practice for Intralaboratory Quality Control Procedures and a Discussion of Reporting Low-Level Data," Standard D4210 Annex A4, 1983, pp. 15-16.

Table 1. Single-Operator Precision and Bias for Sulfate Determined from Analyte Spikes of Wet Deposition Samples.

Analyte	Amount Added, mg/L	n[a]	Mean Percent Recovery	Mean Bias, mg/L	Standard Deviation, mg/L	Statistically Significant Bias?[b]
Sulfate	1.0	10	100.1	0.0	0.1	No
	2.6	9	107.3	0.2	0.1	No

a. Number of replicates
b. 95% Confidence Level

Table 2. Single-Operator Bias and Precision for Sulfate Determined from Quality Control Check Samples.

Theoretical Concentration, mg/L	Measured Concentration, mg/L	n[a]	Bias, mg/L	Bias, %	Precision, s, mg/L	Precision, RSD, %
0.94	0.90	170	-0.04	-4.2	0.06	6.7
7.20	7.13	172	-0.07	-0.97	0.11	1.5

The above data were obtained from records of measurements made under the direction of the NADP/NTN quality assurance program.

a. Number of replicates

Figure 1. Percentile Concentration Values Obtained from Wet Deposition Samples: Sulfate

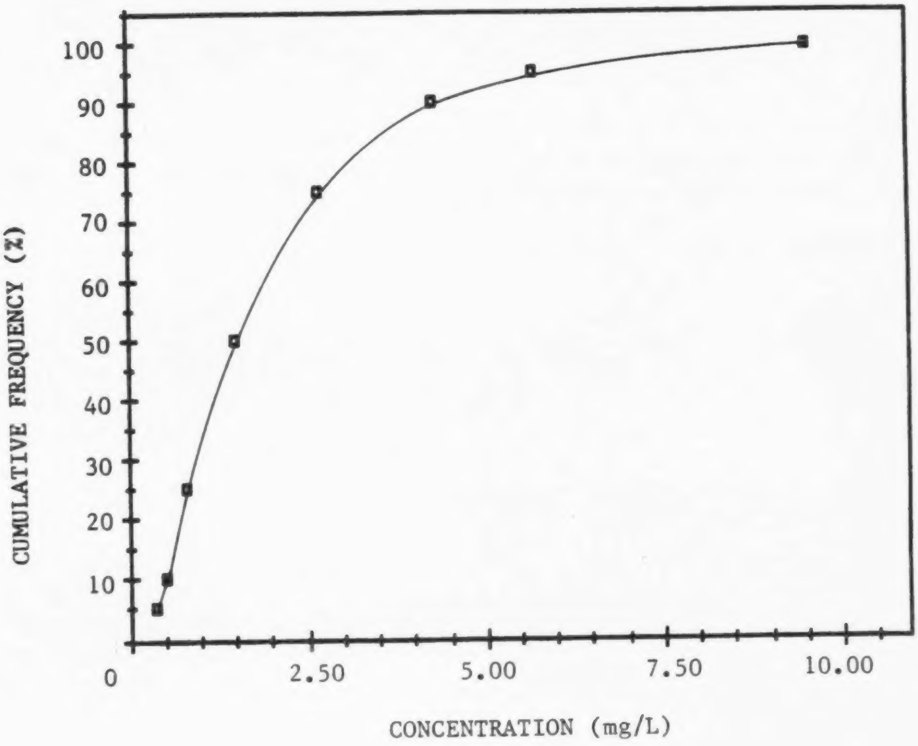
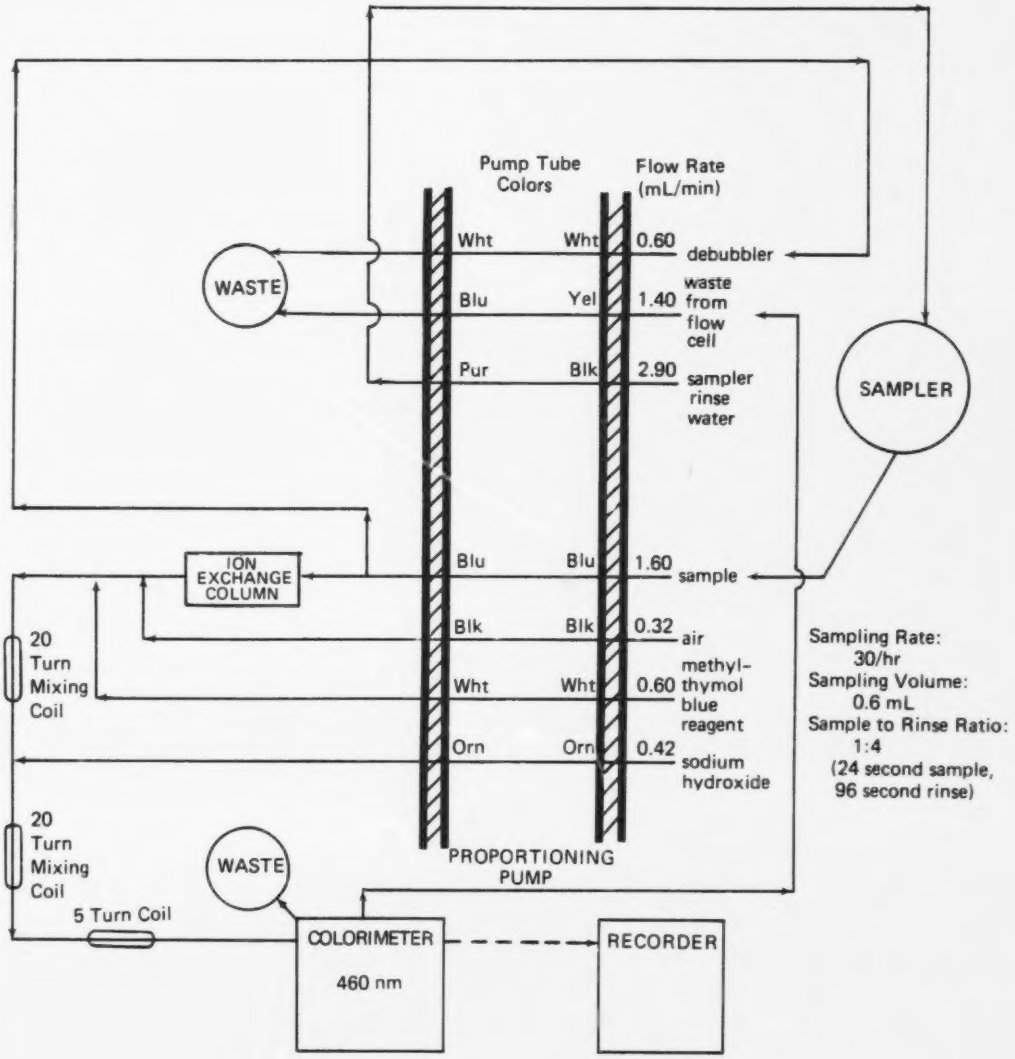


Figure 2. Sulfate Sampling and Analytical System -- Segmented Flow.


Pump Tube Colors
Flow Rate (mL/min)
WASTE
Wht
Wht
0.60
debubbler
Blu
Yel
1.40
waste from flow cell
Pur
Blk
2.90
sampler rinse water
SAMPLER
ION EXCHANGE COLUMN
Blu
Blu
1.60
sample
Blk
Blk
0.32
air
20 Turn Mixing Coil
Wht
Wht
0.60
methyl-thymol blue reagent
Orn
Orn
0.42
sodium hydroxide
20 Turn Mixing Coil
WASTE
PROPORTIONING PUMP
5 Turn Coil
COLORIMETER
460 nm
RECORDER

Sampling Rate:
30/hr
Sampling Volume:
0.6 mL
Sample to Rinse Ratio:
1:4
(24 second sample, 96 second rinse)